A sulfur and halogen budget for the large magmatic system beneath Taupō volcano

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Abstract
The transport and degassing pathways of volatiles through large silicic magmatic systems are central to understanding geothermal fluid compositions, ore deposit genesis, and volcanic eruption dynamics and impacts. Here, we document sulfur (S), chlorine (Cl), and fluorine (F) concentrations in a range of host materials in eruptive deposits from Taupō volcano (New Zealand). Materials analysed are groundmass glass, silicic melt inclusions, and microphenocrystic apatite that equilibrated in shallow melt-dominant magma bodies; silicic melt and apatite inclusions within crystal cores inferred to be sourced from deeper crystal mush; and olivine-hosted basaltic melt inclusions from mafic enclaves that represent the most primitive feedstock magmas. Sulfur and halogen concentrations each follow distinct concentration pathways during magma differentiation in response to changing pressures, temperatures, oxygen fugacities, crystallising mineral phases, the effects of volatile saturation, and the presence of an aqueous fluid phase. Sulfur contents in the basaltic melt inclusions (~2000 ppm) are typical for arc-type magmas, but drop to near detection limits by dacitic compositions, reflecting pyrrhotite crystallisation at ~60 wt. % SiO2 during the onset of magnetite crystallisation. In contrast, Cl increases from ~500 ppm in basalts to ~2500 ppm in dacitic compositions, due to incompatibility in the crystallising phases. Fluorine contents are similar between mafic and silicic compositions (<1200 ppm) and are primarily controlled by the onset of apatite and/or amphibole crystallisation and then destabilisation. Sulfur and Cl partition strongly into an aqueous fluid and/or vapour phase in the shallow silicic system. Sulfur contents in the rhyolite melts are low, yet the Oruanui supereruption is associated with a major sulfate peak in ice core records in Antarctica and Greenland, implying that excess S was derived from a pre-eruptive gas phase, mafic magma recharge, and/or disintegration of a hydrothermal system. We estimate that the 25.5 ka Oruanui eruption ejected >130 Tg of S (390 Tg sulfate) and up to ~1800 Tg of Cl, with potentially global impacts on climate and stratospheric ozone.

Keywords Volatiles · Rhyolite · Sulfur · Chlorine · Fluorine · Fluids · Magma · Petrology · Melt inclusions · Caldera

Introduction
Silicic caldera volcanoes generate some of the largest eruptions on Earth and are fed by magmatic reservoirs that span the crust (Hildreth 1981; Bachmann and Huber 2016; Cashman et al. 2017; Wilson et al. 2021a). In the mid-to-upper crust, evolved silicic magmas (i.e., dacites to rhyolites) are typically stored in a crystal-rich mushy state, from which crystal-poor melt(s) are extracted and accumulated prior to eruptions (Bachmann and Bergantz 2004, 2008; Hildreth 2004; Hildreth and Wilson 2007; Bachmann and Huber 2016). Heat from these crustal magmatic systems also drives vigorous hydrothermal convection, carrying and redistributing metals and volatiles through the enveloping crust and to the surface (Elston 1994; Chambefort and Stefánsson 2013).
2020). However, these silicic magmatic systems are ultimately driven by the thermal and chemical flux from an extensive underlyng column of intruded materials of less-evolved compositions, trending towards primitive basaltic mantle-derived melts (Smith 1979; Hildreth 1981; Annen et al. 2006; Barker et al. 2020). Knowledge of the deeper roots of the magmatic systems is thus vital for understanding the chemical evolution of magmas, the magmatic processes that occur at depth, and surface hydrothermal fluid and gas fluxes.

Constraining the behaviour of volatile components (e.g., H₂O, CO₂, S, Cl, and F), from the mafic roots through to the shallow evolved silicic reservoirs, is critical to understand large silicic magmatic systems. Because of their decreasing solubility in silicate melts with reducing pressure and their incompatibility in most magmatic minerals, these components typically exsolve to form a separate fluid or vapour phase as magmas ascend and crystallise (Edmonds and Wallace 2017). Formation of this volatile phase exerts important controls on a host of geological processes, from hydrothermal mineralisation and metasomatism to the buoyant ascent and fragmentation of magma (Mungall 2003; Webster and Botcharnikov 2011; Edmonds and Wallace 2017). Setting aside H₂O and CO₂, the most abundant and geochemically relevant volatiles are S, Cl, and F. These three elements are important for understanding ore formation, because they strongly influence the partitioning of metals between melts and exsolved vapour or hypersaline brines (Zhu and Sverjensky 1991; Sillitto and Hedenquist 2003; Webster 2004; Wallace and Edmonds 2011). For example, many ore metals display a strong affinity for sulfide hosts (e.g., immiscible sulfide liquids: Mungall 2003; Webster and Botcharnikov 2011; or S complexes with gold: Seward and Barnes 1997) and aqueous chloride and fluoride complexes (Burnham 1979; Webster 1997; Webster et al. 1999). In addition, out-gassing of S and halogens during explosive volcanic eruptions can have significant environmental impacts, and may trigger extended periods of hemispheric or global cooling (Devine et al. 1984; Graf et al. 1997; Robock 2000; Sigl et al. 2015).

Despite their importance, constraining the behaviour and abundance of S, Cl, and F in magmas can be challenging, because they are partly or fully degassed from the melt upon eruption (Oppenheimer 2003, and references therein). This is particularly true for S, which is far less soluble in the melt phase than either Cl or F at shallow crustal depths (Scaillet et al. 1998; Wallace and Edmonds 2011; Zajacz et al. 2012). Thus, where direct measurements of syn-eruptive volatile releases (e.g., remote-sensing observations) are not available, petrological analyses of melt and/or fluid inclusions and volatile-bearing minerals (e.g., apatite: Webster and Piccoli 2015) provide the only means of estimating pre-eruptive magmatic volatile budgets. When coupled with textural and compositional constraints on the origins of inclusion-bearing minerals and assessment of possible post-entrapment modifications (e.g., Lowenstern 1995), such analyses offer insights into the pathways of volatile transport and degassing from the mantle to the surface.

Among active silicic magmatic systems, the central Taupō Volcanic Zone (TVZ: North Island, New Zealand) stands out globally for its exceptional productivity and high frequency of large silicic explosive eruptions (Fig. 1a; Houghton et al. 1995; Wilson et al. 1995). Bookending this area, two caldera volcanoes, Taupō and Okataina have been highly active over the last ~ 55 ka, erupting ~ 780 km³ of overwhelmingly rhyolitic magma, most of it in the 25.5 ka ~ 530 km³ Oruanui eruption (Wilson et al. 2009; Dunbar et al. 2017). Taupō volcano has been the focus of numerous recent petrological studies, providing a high-resolution record of magmatic and eruptive processes across the recent lifespan of its evolving large magmatic system (Barker et al. 2021 for overview). However, there is currently a limited understanding of the ways in which S, Cl, and F are transported through this system, from the mantle-derived melts feeding into the lower crust to the shallow silicic reservoir. Here, we present volatile element analyses of melt inclusions and apatite micro-crystals to address this deficiency and constrain the pre-eruptive S, Cl, and F contents of Taupō magmas. We assess the S, Cl, and F budget for Taupō's magmatic system across the different stages of magma differentiation and highlight the range of mechanisms that control the partitioning of these volatiles.

Previous measurements of S in melt inclusions from TVZ rhyolites by electron microprobe (EPMA) have returned values below detection limits (Dunbar et al. 1989; Dunbar and Kyle 1993; Bégué et al. 2015a,b). Measured Cl and F abundances in quartz- and plagioclase-hosted melt inclusions are between 0.2 and 0.3 wt% and 200 and 600 ppm, respectively, for central TVZ high-SiO₂ rhyolites (Dunbar et al. 1989; Hervig et al. 1989; Dunbar and Kyle 1993; Bégué et al. 2015a,b, 2017). The behaviour of H₂O and CO₂ has been documented in the upper, quartz-saturated regions of TVZ magma systems during both pre- and syn-eruptive processes (Liu et al. 2006; Johnson et al. 2011; Barker et al. 2015; Bégué et al. 2015b; Myers et al. 2018, 2019). Importantly, it is inferred that Oruanui (specifically) and Okataina volcano (in general) melts were saturated with a H₂O-dominated fluid phase during quartz crystallisation (Liu et al. 2006; Johnson et al. 2011, 2013; Charlier et al. 2012; Wilson et al. 2012). However, no studies have yet targeted S or halogen contents for the full range of magma compositions erupted from Taupō or used apatite compositions as a tracer of halogen behaviour in TVZ magmas.
Fig. 1 Setting of Taupō volcano. a Map of the Taupō Volcanic Zone (TVZ) in the central North Island of New Zealand (map inset) and its compositional segmentation and active calderas (blue outlines) and faults (black lines) (Wilson et al. 1995). b Structural features of Taupō volcano showing vent sites, faults, and geothermal features, modified from Barker et al. (2021) and references therein. c Schematic scaled cross section from the C to C’ line shown in b displaying the magmatic system and mush zone beneath Taupō volcano, and the sources, depths, and pathways for the variety of magma components involved in the Oruanui eruption. After Allan et al. (2017)
Geological background

Taupō volcanic zone

The TVZ represents the southern termination of the Tonga-Kermadec arc (Cole and Lewis 1981), forming an NNE-trending zone of arc volcanism and rifting from just SSW of Mt. Ruapehu to the offshore Bay of Plenty (Fig. 1a). Extension rates vary along the TVZ from zero just south of Ruapehu, to 8 mm/yr at Taupō and up to 18 mm/yr at the Bay of Plenty coastline (Rowland and Sibson 2001; Wallace et al. 2004; Villamor and Berryman 2006; Seebeck et al. 2014; Villamor et al. 2017). The TVZ is notably segmented with regards to dominant compositions and erupted volumes. To the north and south are ‘normal’ arc segments characterised by andesite to dacite composite cones (Cole et al. 2000; Price et al. 2005; Townsend et al. 2017). Between them lies a 125 × 60 km central segment, characterised by large caldera-related volcanic centres that erupt dominantly silicic (overwhelmingly rhyolitic) magmas. Magma output rates are an order of magnitude higher in this central region than in the other segments (Wilson et al. 1995, 2009; Leonard et al. 2010). The central TVZ is characterised by a thinned crust, active extension, high mantle-derived magma fluxes, extreme heat flow, and abundant geothermal features with discharge of thermal water and gases (Bibby et al. 1995; Giggenbach 1995; Hochstein 1995; Houghton et al. 1995; Price et al. 2005; Bernal et al. 2014; Wilson and Rowland 2016; Bégué et al. 2017; Barker et al. 2020).

Taupō volcano

Taupō is the southernmost caldera volcano in the central TVZ (Fig. 1a). Most of the caldera structure and young vent sites are concealed beneath Lake Taupō (Fig. 1b: Barker et al. 2021). Early activity in the wider Taupō area is mostly constrained by dating of surficial lavas (Leonard 2003; Leonard et al. 2010) or pyroclastic units in deep geothermal drill holes (Chambeafort et al. 2014; Rosenberg et al. 2020; Milicich et al. 2020). Detailed understanding of Taupō is focused around the last ~50 kyr of activity, encompassing the build up to and aftermath of the ~25.5 ka Oruanui supereruption. Eruptions in this period have mostly occurred from two independent silicic magmatic systems: one (by far the larger, and our focus here) spatially overlapping with the Oruanui caldera, and a second focused to the northeast of the modern lake (Sutton et al. 1995; Wilson and Charlier 2009). The Oruanui event discharged ~530 km$^3$ of rhyolite magma (> 1100 km$^3$ of pyroclastic material) in a prolonged, multi-phase eruption (Wilson 2001; Wilson et al. 2006; Allan et al. 2017). Recognition of Oruanui glass shards accompanied by a major non-sea-salt sulfate anomaly in an Antarctic ice core (Dunbar et al. 2017) implies that ash and aerosol dispersal was at least hemispheric (and possibly global: Svensson et al. 2020; Lin et al. 2022). Post-Oruanui activity at Taupō (Wilson 1993) resumed with three dacitic eruptions from ~20.5–17 ka from vents in northern Lake Taupō (units Ψ, Ω, Α). From ~12 ka, 25 rhyolite eruptions occurred from vent sites mostly now concealed beneath the lake. These rhyolites are subdivided into three subgroups (SG1-3) erupted from 11.8 to 9.95 ka (SG1: units B-E), 7.05 to 2.75 ka (SG2: units F-W), and 2.15 to 1.8 ka (SG3: units X–Z) (Sutton et al. 2000; Barker et al. 2015).

Young eruptive products of Taupō

We focus here on eruptive products from the Taupō magmatic system during and after the Oruanui eruption. High-silica rhyolite (HSR; > 74 wt% SiO$_2$) comprises more than 98% of the erupted Oruanui magma by volume, but a subordinate volume of low-silica rhyolite (LSR; < 74 wt% SiO$_2$) was also tapped (Wilson et al. 2006; Allan et al. 2017). The crystal-poor HSR contains 3–13 wt% crystals of plagioclase + quartz + orthopyroxene + hornblende + magnetite + ilmenite + accessory apatite and zircon (Allan et al. 2017). It is inferred to represent a large melt-dominant magma body, formed by rapid extraction of interstitial melt plus some crystals from a mafic source, followed by limited additional crystal growth (Allan et al. 2013, 2017; Fig. 1c). The LSR is inferred to represent aliquots of interstitial melt from the upper regions of the mush zone that were syn-eruptively tapped. Compositional similarities among pumice clasts (and uniformity within analytical error of the groundmass glass compositions) sampled from each of the eruptive phases indicates that the HSR magma was held in a well-mixed, actively convecting magma body immediately prior to evacuation, at minimum depths of 4–7 km (Wilson et al. 2006; Allan et al. 2017; Myers et al. 2018, 2019). However, 90% of the orthopyroxene and plagioclase crystals have cores with disequilibrium textures and compositions that are not in equilibrium with the HSR melt. These features are inferred to reflect inheritance of these cores from diverse sources within the deeper mush zone (Allan et al. 2017; Fig. 2a, b).

In addition, two independent mafic magmas (tholeiitic and olivine-bearing calc-alkaline) were erupted, together representing about 1% of the erupted Oruanui magma (Wilson et al. 2006; Allan et al. 2017; Rooyakkers et al. 2018). Syn-eruptive interactions between the mafic magmas and Oruanui rhyolite occurred in a rheological transition zone between the rigid crystal mush and the melt-dominated body (Rooyakkers et al. 2018). Notably, these mafic enclaves carry high-Mg# (Fo$_{85-87}$) olivines that represent the most primitive basaltic magmas feeding into the crust beneath the region (Barker et al. 2020; Fig. 2c, d).

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The three post-Oruanui dacites contain up to 25 wt% crystals (plagioclase + clinopyroxene + orthopyroxene + magnetite + ilmenite + accessory apatite + occasional sulfide inclusions: Fig. 2e). Crystal textures and compositions in the dacites imply that they originate from depths of > 8 km at temperatures of > 900 °C (Gelman et al. 2013; Barker et al. 2015). From 12 ka onwards, erupted rhyolites reflect rebuilding of a shallow (4–8 km depth) silicic reservoir, with step-wise changes in composition between the three magma subgroups reflecting subtle changes in mineral compositions.
stability (Barker et al. 2014, 2015). Post-Oruanui rhyolites have low crystal contents (mostly <5–7 wt. %): all contain plagioclase + orthopyroxene + magnetite + ilmenite + accessory apatite and zircon, while SG1 eruptives also contain clinopyroxene and hornblende. Post-Oruanui rhyolites are 20–70 °C hotter than the Oruanui HSR, but are inferred to have resided at a broadly similar depth in the crust (Barker et al. 2014, 2015; Wilson et al. 2021b). Mafic recharge remained important, as juvenile mafic enclaves are found in the 3.5 ka Unit S (Waimihia) deposits (Blake et al. 1992), while reversely zoned crystals in the 1.8 ka Taupō (Unit Y) deposits indicate pre-eruptive heating linked to mafic input only a few decades before eruption (Barker et al. 2015, 2016).

Methods

Sample selection

Samples investigated cover a broad range of magma compositions, representing the deep to shallow magmatic system beneath Taupō volcano. For the upper level silicic part of the system, three LSR and seven HSR clasts from the Oruanui ignimbrite (eruptive phase 10 of Wilson 2001) were selected. Five post-Oruanui eruptive units were sampled: dacite units Ψ and Ω, and three rhyolite eruptions including units C, S (Waimihia) and Y (Taupō), which cover the compositional range of the Holocene events (Table 1). All samples were crushed, sieved, and picked for minerals containing melt and/or apatite inclusions. We especially targeted orthopyroxenes, because they host abundant glassy melt and apatite inclusions. Melt inclusions from Oruanui LSR samples are typically from more Mg-rich orthopyroxene crystals with higher-Al cores, interpreted to be derived from deeper parts of the silicic mush system (Allan et al. 2017; Fig. 1c, 2b). To constrain volatile abundances in the basaltic melts feeding into the system, olivines (Fo85-87) with melt inclusions were used to model the equilibrium olivine−melt−mush system (Roeder and Emslie 1970, assuming Fe3+/FeTotal = 0.15). Melt inclusions hosted in normally zoned orthopyroxene cores were analysed by EPMA, along with groundmass glass adhering to the crystal exterior. For glass major element analyses, we used a 15 kV accelerating voltage and 8 nA beam current with a 10 µm circular beam, and count times of 30 s on peak and 15 s on background for most elements. For Na, the peak search was skipped and count times were shorter at 10 s on peak and 5 s on background to minimise Na losses. For volatile elements, a second analysis was performed using a 60 nA current and counting times of 60 s on peak and 30 s on background for S and Cl and 120 s on peak for F. For F analyses, the peak search was skipped and the following conditions were specified after Witter and Kuehner (2004): peak position = 87.007, gain = 4, Hv [V] = 1830, base level [V] = 0.5, window [V] = 3.00, diff. Due to the interference of the Fe-induced X-ray lines, a suite of secondary standards (ferrobasalt, high-Mg basalt, andesite, MORB, rhyodacite, rhyolite) with known Fe and F values was used to correct the raw EPMA data (Zhang et al. 2016). Melt inclusions hosted in olivine were analysed using the same procedure as for rhyolite glasses, but with a different suite of calibrating and secondary standards. Measured glass compositions were corrected for post-entrapment crystallisation and olivine-melt re-equilibration (Barker et al. 2020) by incrementally adding or removing olivine until an equilibrium KD(Fe–Mg)olivine−melt value of 0.3 was reached (Roeder and Emslie 1970, assuming Fe3+/FeTotal = 0.15). Melt inclusions with S concentrations lower than the expected Fe-sulfide saturation level (Wallace and Carmichael 1992) were considered to be degassed and were set aside.

Orthopyroxene EPMA analyses were conducted in normally zoned cores immediately adjacent to already analysed melt inclusions using a focused beam, 12 nA current, 15 kV accelerating voltage, 30 s peak and 15 s background counting times, and a narrow peak search. Microphenocryst and orthopyroxene-hosted apatite crystals were analysed for major and volatile element contents by EPMA using a diffuse 10 µm beam, 4 nA current, 10 kV accelerating voltage, and a narrow peak search. Care was taken to minimise exposure of samples to the beam during the programming of analytical points to avoid mobilising volatile elements. Sulfides hosted as inclusions in orthopyroxene cores were analysed for major element contents using a 1 µm beam, 60 nA current, 15 kV accelerating voltage, 30 s peak and 15 s background counting times, and a narrow peak search (after Liu et al. 2018).

Trace elements

Glass, orthopyroxene, and apatite trace-element analyses were conducted using a Resonetics S155-SE (193 nm)
Eximer laser coupled to an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS) at Victoria University of Wellington. ICP-MS tuning and optimisation of signal sensitivity and stability was achieved prior to sample analysis by rastering across the primary standards and adjusting the flow of ultra-pure He gas. Rhyolite glass NIST SRM612 was analysed after every ten samples and used as the calibration standard. Glass and orthopyroxene analyses were performed with a 35 μm circular laser beam pulsed at 10 Hz for 30 s. Apatites were analysed using the same configuration, but acquisition times varied from 20 to 30 s depending on the size of the crystal. All analyses were separated by 60 s of background measurement. Raw ICP-MS data were processed with Iolite (Hellstrom et al. 2008), using 29Si as the internal standard for glass and orthopyroxene and 42Ca for apatite. Repeat analyses of secondary standards NIST610 and NIST 612 (Table A1.2) indicate analytical precision (2σ) < 15% relative for most trace elements, excluding the Rare-Earth Elements (REEs) and Ta (20–30%). Accuracy is better than ± 10% for most elements (Online Resource 1).

Table 1 Average major and volatile element compositions of Taupō glass (GG) and melt inclusions (MI)

| Eruption Type | Oruanui HSR | Oruanui LSR | Unit Ψ | Unit Ω | C | S | Y | Oruanui S |
|---------------|-------------|-------------|--------|--------|---|---|---|----------|
| Age (ka)      | 25.5        | 25.5        | 20.5   | 18.8   | 11.4 | 3.6 | 1.8 | 25.5     |
| Analysis position | MI | GG | MI | GG | MI | MI | GG | MI | MI |
| n             | 91          | 95          | 88     | 23     | 7  | 20 | 8  | 4  | 3  | 3  | 2  | 25  | 54  | 9  | 5  |

| Oxide abundances (wt. %) | SiO2 | TiO2 | Al2O3 | FeO | MnO | MgO | CaO | Na2O | K2O | Total | σ  |
|--------------------------|------|------|-------|-----|-----|-----|-----|------|-----|-------|----|
|                          | 77.26| 0.13 | 12.79 | 1.62| 0.24| 0.12| 1.02| 3.52 | 3.46| 95.21 | 0.17|
|                          | 77.70| 0.11 | 12.57 | 1.43| 0.17| 0.12| 1.08| 3.81 | 3.61| 98.73 | 0.24|
|                          | 75.75| 0.23 | 13.20 | 2.34| 0.06| 0.25| 1.45| 4.02 | 2.77| 95.12 | 0.06|
|                          | 74.97| 0.25 | 13.39 | 2.91| 0.09| 0.58| 1.48| 3.80 | 3.30| 95.88 | 0.17|
|                          | 72.72| 0.51 | 14.35 | 2.19| 0.09| 0.53| 1.46| 3.80 | 3.06| 96.81 | 0.05|
|                          | 72.23| 0.48 | 14.61 | 3.03| 0.07| 0.47| 1.46| 4.41 | 3.30| 98.89 | 0.14|
|                          | 72.98| 0.47 | 14.07 | 2.84| 0.06| 0.47| 1.38| 4.31 | 3.06| 98.40 | 0.23|
|                          | 75.80| 0.47 | 13.44 | 1.94| 0.13| 0.17| 1.28| 4.01 | 3.00| 95.45 | 0.35|
|                          | 76.08| 0.17 | 13.27 | 1.76| 0.18| 0.17| 1.10| 3.99 | 2.96| 98.84 | 0.07|
|                          | 75.44| 0.18 | 13.51 | 2.30| 0.02| 0.20| 1.01| 3.81 | 2.87| 96.32 | 0.06|
|                          | 76.18| 0.18 | 13.20 | 1.93| 0.20| 0.16| 0.51| 4.10 | 2.83| 98.78 | 0.12|
|                          | 76.18| 0.18 | 13.28 | 2.38| 0.15| 0.15| 0.35| 3.89 | 2.87| 96.62 | 0.03|
|                          | 75.60| 0.23 | 15.69 | 1.71| 0.19| 0.24| 0.51| 4.25 | 1.88| 96.64 | 0.13|
|                          | 75.23| 0.25 | 15.19 | 1.01| 0.19| 0.22| 0.42| 1.70 | 0.36| 96.62 | 0.10|
|                          | 49.05 | 0.34 | 16.01 | 0.64| 0.39| 0.09| 1.07| 1.88 | 1.70| 92.97 | 0.39|
|                          | 49.87 | 0.28 | 16.17 | 0.39| 0.39| 0.09| 1.04| 1.70 | 1.88| 92.11 | 0.39|

| Volatiles (ppm) | S | σ | F | σ | Cl | σ | σ | Cl | σ |
|-----------------|---|---|---|---|----|---|---|----|---|
|                 | 33 | 13 | 479 | 127 | 2042 | 207 | 28 | 19 | 8 |
|                 | 28 | 12 | 591 | 132 | 2035 | 166 | 62 | 19 | 8 |
|                 | 62 | 17 | 614 | 91  | 1826 | 92  | 79 | 17 | 5 |
|                 | 102| 25 | 636 | 86  | 1776 | 82  | 51 | 14 | 4 |
|                 | 79 | 25 | 758 | 48  | 2044 | 293 | 56 | 36 | 13 |
|                 | 51 | 5  | 687 | 38  | 1958 | 143 | 53 | 28 | 10 |
|                 | 54 | 1  | 601 | 16  | 1649 | 140 | 54 | 19 | 6  |
|                 | 30 | 2  | 675 | 8   | 1768 | 30  | 49 | 18 | 3  |
|                 | 49 | 2  | 720 | 33  | 1800 | 130 | 29 | 12 | 2  |
|                 | 29 | 2  | 633 | 18  | 1879 | 100 | 30 | 8  | 1  |
|                 | 1397 | 147 | 567 | 57  | 1908 | 134 | 1587 | 25 | 61 |

Oxide abundances normalised to 100 % on a volatile free basis, with original analytical totals given. Eruption ages are given in years before present and sourced from Wilson (1993) and Dunbar et al. (2017). See Online Resource 1 for all raw data and standards.
Results

Mafic melt compositions

The olivine-hosted melt inclusions are among the least-evolved compositions documented in the TVZ, with > 10 wt% MgO (Table 1: Barker et al. 2020). They represent primitive melts feeding into deeper parts of the crustal magmatic system that were fortuitously carried through to the surface uncontaminated. Sulfur contents of these melt inclusions are typical for arc basalts at ~ 1000–2000 ppm (Fig. 3a). Chlorine contents are considerably lower than in the silicic magmas at 500–1000 ppm, with little difference between the Oruanui and Unit S (Waimihia) inclusions (Fig. 3b). In contrast, F contents are similar to the silicic magmas at ~400–700 ppm (Fig. 3c).

Silicic melt compositions

Glass compositions for the Oruanui and post-Oruanui samples plot within the published range of values for glass separates or melt inclusions from the corresponding units (Fig. 4; Table 1; Sutton et al. 1995, 2000; Liu et al. 2006; Wilson et al. 2006; Allan et al. 2013, 2017; Barker et al. 2015; Myers et al. 2018, 2019). The only differences between melt inclusion and groundmass glass major oxide compositions for the silicic units occur for Al2O3 and FeOT (and K2O for the Oruanui HSR), for which groundmass glass values are lower. Silicic melt inclusion compositions vary as expected with their host crystal compositions, such that inclusions hosted in orthopyroxenes with higher enstatite and Al contents have lower SiO2 contents (Fig. 5).

Sulfur contents in silicic melt inclusions and groundmass glasses are always < 150 ppm and commonly near detection limit (~ 10 ppm) for the Oruanui (average ~ 30 ppm) and post-Oruanui rhyolites (average ~ 50 ppm), consistent with previous studies (Fig. 3d). Chlorine abundances are variable but mostly cluster between ~1500–2500 ppm for the silicic melts, with relatively consistent levels between the dacites and rhyolites (Fig. 3e). However, average Cl contents in Oruanui HSR melt inclusions are slightly higher and show a negative correlation with SiO2. Fluorine contents are also scattered but overall show a weak negative correlation with SiO2, mainly clustering between ~600–900 ppm for the dacites and ~300–1000 ppm for the rhyolites (Fig. 3f). Fluorine in Oruanui HSR melt inclusions increases with increasing SiO2 and is slightly higher on average in the groundmass glass, whereas, in contrast, the dacites have lower F contents in the groundmass glass relative to melt inclusions. Compatible trace elements, such as Sr and Y, correspond weakly with changing S, Cl, and F contents for the different magma types largely depending on the presence or absence of amphibole (Fig. S1).

Apatite chemistry

Apatites in the Taupo silicic magmas typically have XF ap from 0.4 to 0.57, XCl ap from 0.1 to 0.19 and XOH ap from 0.3 to 0.46 (with a stoichiometric volatile site sum of 1.0 calculated as Ca(PO4) (OH,F,Cl): Fig. 6a). The volatile contents of the apatites are distinct for the different magma types sampled (Fig. 6b). Notably, Oruanui HSR apatites typically have higher XCl/XOH than the other magma types, and groundmass apatite in both the HSR and LSR have elevated XF/XOH compared to those hosted in orthopyroxene. SO3 contents of apatites are low (< 0.1 wt.% and commonly below detection limit: Online Resource 1).

Due to the small size of the apatite crystals (typically < 30 µm width), only a limited number of trace-element analyses could be obtained for the Oruanui HSR and LSR. These analyses reveal highly variable trace-element contents ranging from approximately 300–1300 ppm Na, 500–1100 ppm Mg, 1000–2100 ppm Mn, 300–700 ppm Sr and with high levels of REEs including 650–1300 ppm La, 1400–2900 ppm Ce, and 1200–1900 ppm Nd (Online Resource 1). Some trace-element contents differ between the LSR and HSR, consistent with their distinct volatile contents (Fig. S2). For example, higher XCl/XF apatites from the Oruanui HSR have higher REE contents than LSR apatites, but lower Sr, Mn, and Mg.

Sulfide chemistry

Sulfide inclusions are present in pyroxenes from the post-Oruanui dacites, commonly in crystal cores or in melt inclusions along with abundant Fe–Ti oxides. Due to the small size (< 10–20 µm) of these inclusions, only five successful EPMA analyses could be acquired. These data cluster at relatively constant Fe and more variable S mol values within the range that defines the pyrrhotite chemical formula Fe1−xS, where 0 < x < 0.2 (Fig. S3).

Discussion

By including components from the melt-dominant silicic magma bodies that feed eruptions at Taupō (e.g., quartz-hosted melt inclusions and groundmass apatite), the deeper mush bodies from which they are derived (e.g., apatite- and melt inclusions hosted in inherited orthopyroxene cores), and the primitive mafic magmas that drive the system at depth (high-Fo olivine-hosted melt inclusions), our data allow us to explore the abundances and behaviour of S, Cl,
Fig. 3 Sulfur and halogen contents versus SiO$_2$ for melt inclusions (MI) and groundmass glass (GG) from Taupō volcano. a Sulfur versus SiO$_2$ for olivine-hosted basaltic MI compared with the Oruanui eruption high- and low-silica rhyolites (HSR and LSR, respectively), and the post-Oruanui dacites and rhyolites (P-Ou Dac and P-Ou Rhy, respectively). Inset panel show by grey box. Previous olivine MI data are from Barker et al. (2020). b Chlorine versus SiO$_2$: details as in panel a. c Fluorine versus SiO$_2$: details as in panel a. d Zoomed-in panel from a showing S data in more detail for orthopyroxene-hosted MI and GG from the silicic magmas with previously published data from plagioclase and/or quartz and/or orthopyroxene-hosted inclusions represented by coloured fields (pink = post-Oruanui subgroup 3 rhyolite compositions; blue = HSR: Dunbar et al. 1989; Hervig et al. 1989; Dunbar and Kyle 1993; Bégéé et al. 2015a, 2015b, 2017). Trend lines shown in inset panels are linear regressions of each corresponding melt inclusion population. e Zoomed-in panel from b showing Cl data: details as in d. f Zoomed-in panel from c showing F data: details as in d. Error bars represent 2 s.d. errors based on repeat analyses of VG-568 (S and Cl) and VG-A99 (F). Detection limits for S and F are denoted by dashed horizontal lines. The Cl detection limit is below the presented vertical axis values. All data and standards presented in Online Resource 1.
and F in both the upper reaches and mafic roots of the Taupō magmatic system. However, as is common in arc volcanoes (e.g., Reubi and Blundy 2009), the lack of compositionally intermediate melt inclusions in our dataset makes it challenging to directly track the abundance of volatiles along any line of descent from the parental source magmas to their silicic derivatives. To address this issue, we consider other published lines of evidence that offer constraints on the behaviours of S, Cl, and F during magma differentiation beneath Taupō.

**Key inferences from textural and petrologic studies**

The Oruanui HSR and post-Oruanui dacites were targeted in this study due to their high proportions of inherited (dominantly less-evolved) cores in major mineral phases (Charlier et al. 2008; Allan et al. 2013, 2017; Barker et al. 2015). For
example, Allan et al. (2013, 2017) inferred that the compositionally diverse Oruanui orthopyroxene cores reflected crystallisation from a range of hotter and more primitive melts within a compositionally stratified mush, whereas the near-homogeneous rims crystallised from the melt-dominant HSR body that was extracted from this mush and erupted (Wilson et al. 2006; Allan et al. 2017). Crystallisation pressures for these mush-derived cores were inferred to be up to at least 250 MPa (from geobarometry using co-crystallising hornblende: Allan et al. 2013, 2017). We observe close compositional overlap between our Oruanui orthopyroxene data and those of Allan et al. (2013), and thus infer that the Oruanui orthopyroxene cores considered here, and the melt- and apatite inclusions that they enclose (Fig. 2), were also derived from the compositionally stratified mid- to upper crustal Oruanui mush. The most primitive melt inclusions are inferred to sample the deeper and more mafic regions of this mush, whereas more-evolved inclusions are inferred to sample its shallower regions. The correlation between host En values and their melt inclusion SiO$_2$ contents (Fig. 5a) supports this inference. We interpret the variability of crystal core and melt-inclusion compositions in the post-Oruanui dacites as recording similar vertical compositional stratification within a rebuilding silicic mush system (Barker et al. 2015).

In contrast to the orthopyroxene-hosted apatites from the mush column, microphenocryst apatites are inferred to have grown in and/or equilibrated with the shallower melt-dominant bodies in which they were erupted. Apatite is the only phase in Taupō magmas to accommodate phosphorous in appreciable amounts. A compilation of intermediate-to-rhyolitic whole-rock data from Taupō volcano shows an enrichment-depletion trend for P$_2$O$_5$ versus SiO$_2$ (Fig. 7). The hinge point at ~ 57 wt% SiO$_2$ is here inferred to represent the onset of apatite crystallisation, after which P$_2$O$_5$ is progressively depleted in the melt. The continuous stability of apatite beyond this hinge point is supported by its ubiquitous presence as both crystal-hosted inclusions and microphenocrysts in all andesitic-to-rhyolitic Taupō magmas (Hervig et al. 1989; Sutton et al. 1995, 2000; Wilson et al. 2006; Gelman et al. 2013; Barker et al. 2015). However, we note a wide range in P$_2$O$_5$ contents for mafic enclaves with intermediate compositions that likely result from crystal accumulation, rather than reflecting true liquid melt compositions (Allan et al. 2017; Rooyakkers et al. 2018).

**Behaviour of sulfur**

There is a large disparity between the S contents of basaltic (up to ~ 2000 ppm) and silicic (dacitic to rhyolitic: < 200 ppm S, trending down to below the detection limits) melt inclusions. Here, we explore the origin of this disparity and discuss the processes that may influence the magmatic S budget at Taupō.

**Sulfur saturation in the deep mafic system**

Because of its incompatibility, S contents of basaltic melts increase during crystallisation until saturation with, and subsequent separation of, a non-volatile S-rich phase (SRP, e.g., immiscible liquid, sulfate or sulfide: Webster and Botcharnikov 2011). Sulfur saturation is strongly influenced by the oxygen fugacity (f$_{O2}$) and associated oxidation state of the melt via its strong control on S speciation (Carroll and Rutherford 1985, 1987; Clemente et al. 2004; Behrens and
Gaillard 2006; Baker and Moretti 2011; Jugo et al. 2005a,b; Jugo 2009; Webster and Botcharnikov 2011; Zajacz et al. 2012). Sulfur solubility increases considerably with increasing $f\text{O}_2$ as the dominant S ion transitions from sulfide ($\text{S}^{2-}$) to sulfate ($\text{S}^{6+}$). Typically, this transition occurs near the nickel–nickel oxide (NNO) redox buffer (Webster and Botcharnikov 2011 and references therein). With increasing melt polymerisation and decreasing temperature (both to be expected for an ascending magma following a typical differentiation pathway), the maximum S content required to achieve saturation decreases (Fincham and Richardson 1954; Wendlandt 1982; Liu et al. 2007).

Temperature and $f\text{O}_2$ estimates for Taupō magmas are derived from Fe–Ti oxide pairs (Fig. 8; Barker et al. 2015; Allan et al. 2017). The mafic magmas are hotter and more oxidised than their felsic counterparts: for example, ~1100 °C and NNO +1 for the Oruanui and Unit S (Waimihia) mafic magmas versus ~800 to 900 °C and NNO to NNO +0.8 for the dacites and rhyolites (Barker et al. 2015; Allan et al. 2017). Pressure estimates from amphibole inclusion compositions for orthopyroxene-hostedapatites and average groundmass glass for the loose apatite crystals. Equilibrium calculated at 790 °C for HSR groundmass, 820 °C for HSR opx-hosted, 840 °C for LSR groundmass and opx-hosted, 900 °C for the dacites, 860 °C for SG3 and 830 °C for SG2 rhyolites. The 1:1 black dotted line represents equilibrium and the black dashed line represents the accepted uncertainty of 30% in ApThermo (Li and Costa 2020). All data and standards are presented in Online Resource 1.

There is a broad range in the S content of olivine-hosted melt inclusions in arc basaltic magmas: most are 900–2500 ppm (Wallace and Edmonds 2011), extending beyond the range in the Taupō basaltic inclusions (maximum ~2100 ppm: Fig. 3a). As the majority of arc mafic magmas have water contents too low for aqueous fluid saturation at deep crustal levels (e.g., Webster 2004; Shishkina et al. 2010), the upper limit of arc basalt S contents probably reflects saturation with a sulfur rich phase (SRP). It is thus likely that the S contents of the most evolved basaltic melts at Taupō are nearing sulfur saturation, after which an SRP would form. The lack of anhydrite as either inclusions or phenocrysts in eruptives from Taupō suggests that the magmas are generally too reducing to stabilise anhydrite (Clemente et al. 2004). This is consistent with the low S
levels measured in both orthopyroxene-hosted and groundmass apatite microphenocrysts (cf. Parat and Holtz, 2005).

Sulfide depletion event

The Taupō silicic magmas considered here contain sufficient FeO$_T$ to support sulfide saturation (Fig. 4), and pyrrhotite occurs as accessory inclusions in inherited crystal cores within the post-Oruanui dacites. Thus, sulfide saturation must occur at some intermediate point on the liquid line of descent between the S-undersaturated basaltic melts and dacitic compositions. Constraining whether the pyrrhotite sampled by the post-Oruanui dacites is stable across intermediate compositions is challenging given the lack of representative melt inclusions in basaltic-to-andesitic magmas erupted from Taupō. However, textural studies of intermediate magmas have proposed that sulfide-rich phases are commonly converted to iron oxide minerals, likely due to shallow pre-eruptive degassing of S (Larocque and Stimac 2000; Wallace and Edmonds 2011). Thus, we cannot rule out the presence of sulfide in basaltic-to-andesitic Taupō melts. To better constrain the timing of sulfide crystallisation, we consider whole-rock trends for selected major oxides, which can be used to infer crystallisation events that may influence the stability of any sulfide phases.

In this regard, one explanation for the appearance of trace pyrrhotite in the Taupō dacites is the ‘magnetite crisis’ (Jenner et al. 2010), where there is correlation between the onset of magnetite crystallisation and a sharp depletion of S and associated chalcophile elements in the melt. The selective depletion of only some chalcophile elements (Cu, Au, Ag) during this event has been linked with crystallisation of a sulfide phase (Jenner et al. 2010), triggered by a change in fO$_2$ and Fe$^{3+}/\Sigma$Fe in the melt as magnetite begins to crystallise. The high compatibility of Ti in magnetite allows it to be used as a proxy to identify the magnetite crisis. Initially incompatible, TiO$_2$ increases with SiO$_2$ to a hinge point marking the onset of magnetite crystallisation at ~57 wt% SiO$_2$ (Fig. 7a) after which it decreases (cf. 60% SiO$_2$ in Jenner et al. 2010). We infer that the onset of magnetite crystallisation in the Taupō magmas changed the fO$_2$, lowering sulfide solubility and triggering extensive pyrrhotite crystallisation. Subsequent pyrrhotite growth (Fe$_{1-x}$S; ~39 wt% S)
and fractional crystallisation would then significantly deplete the melt S content (e.g., to less than 150 ppm: Fig. 3d). P2O5 values also serve as a proxy for the onset of apatite crystallisation, with a hinge point also at ~57 wt% whole-rock SiO2 (Fig. 7b) (cf. 60% SiO2 in Jenner et al. 2010). Apatite is commonly associated with magnetite in phenocrysts of the Taupō samples (e.g., Ewart 1967; Fig. 2b). The onset of magnetite crystallisation thus appears to trigger apatite crystallisation as well as the precipitation of sulfide.

**Partitioning of sulfur into the aqueous fluid/gas phase in the shallow system**

Pyrrhotite crystallisation is inferred to play a key role in lowering S contents in the intermediate-to-dacite magmas, but little pyrrhotite is observed as inclusions in the rhyolitic magmas. Sulfur contents are consistently <150 ppm in Taupō melt inclusions and groundmass glass at >70 wt. % SiO2 (Fig. 3d). Without pyrrhotite crystallisation occurring, S contents in the melt should increase with melt evolution through to high-SiO2 rhyolite. However, S contents in the melt S content (e.g., to less than 150 ppm: Fig. 3d). P2O5 and fractional crystallisation would then significantly deplete melt S contents to <150 ppm regardless of the sulfur saturation level (Edmonds and Wallace 2017), further depleting melt S contents to <150 ppm (Fig. 3d).

The H2O and CO2 contents of melt inclusions from Taupō indicate that silicic melts were volatile (H2O, CO2) saturated during the crystallisation of quartz and plagioclase at pressures of <150 to 200 MPa (e.g., Liu et al. 2006; Barker et al. 2015; Myers et al. 2018, 2019). Sulfur has been shown to partition strongly from felsic melt into aqueous fluid phases at pressures of ~200 MPa and temperatures of ~800 °C, with experimentally determined fluid/melt partition coefficients ($D_S^{fluid/melt}$) varying from ~50 to 470 (e.g., Keppler 2010; Binder et al. 2018). The strongest control is oxygen fugacity, with relatively oxidised melts exhibiting lower $D_S^{fluid/melt}$ values when compared with relatively reduced melts by nearly an order of magnitude at the same pressures and temperatures (Keppler 2010; Zajacz et al. 2012; Binder et al. 2018). Experimental studies of pumice from the Taupō 1.8 ka eruption yielded $D_S^{fluid/melt}$ of ~27, assuming melt values of 44 ppm S and ~1200 ppm calculated for the aqueous fluid phase (Scaillet et al. 2003; Scaillet and Pichavant 2003). Applying the partition coefficient of Keppler (2010) derived from a haplogranite ($D_S^{fluid/melt}$ ~ 50) of similar major oxide composition to Taupō rhyolites (SiO2 ~ 75 wt%, Al2O3 ~ 11 wt%, Na2O ~ 3.5 wt%, K2O ~ 3.5 wt%) at fo2 of NNO +0.5, 850 °C and 200 MPa yields an estimate of 2000 ppm S in the Oruanui HSR fluid phase at ~75 wt% SiO2. We therefore propose that exsolution of an S-rich aqueous fluid phase at pressures of <200 MPa was the main driver for continuing depletion of S with progressive evolution of Taupō’s silicic melts after the cessation of pyrrhotite crystallisation, thereby maintaining the very low levels of S observed in the Taupō rhyolite melts.

**Summary of sulfur transport below Taupō volcano**

The inferred behaviour of S during the evolution of Taupō magmas is illustrated in Fig. 9. The high S contents in the basaltic melt inclusions (Fig. 3a) reflect their arc setting, the initial crystallisation of S-free minerals, and the absence of an S-bearing fluid or mineral phase (point 1 in Fig. 9). Through continued fractional crystallisation, the basaltic magmas reach S saturation, resulting in the initial formation of an SRP (point 2), which increases in abundance with melt evolution and decreasing S solubility in the melt. Whole-rock SiO2 contents of ~57 wt% (inferred to represent ~60–65 wt% SiO2 in the interstitial silicic melt, based on data from the post-Oruanui dacites: Barker et al. 2015) mark the onset of magnetite crystallisation (point 3), lowering the melt fo2 and triggering an episode of pyrrhotite crystallisation. Melt S contents are inferred to reduce to <200 ppm by the end of pyrrhotite crystallisation. The silicic melts subsequently reach water saturation in the upper crust and an aqueous fluid phase exsolves from the melt (point 4). We infer that sulfur is then partitioned between melt and aqueous fluid regardless of the sulfur saturation level (Edmonds and Wallace 2017), further depleting melt S contents to <150 ppm (Fig. 3d).

**Fig. 9** The inferred pathway for S in the melt (red line, ppm) relative to SiO2 (wt%), between the end-member compositions analysed in this study (see Fig. 3a for data points). Dashed red arrows represent the inferred direction of melt sulfur content during melt evolution prior to saturation. The inferred curve for sulfur saturation is denoted by the dashed black line and the region where an S-rich phase exists is shown by the black dotted area. The grey field denotes the melt SiO2 where extensive pyrrhotite crystallisation occurs. The blue field denotes the saturation of an aqueous vapour phase in the melt. See text for discussion and description of numbered points.
Behaviour of chlorine

There is an apparent enrichment in Cl from the basaltic to silicic Taupō melt compositions (Fig. 3b). This increase is likely to be controlled by two key factors: (1) the incompatibility of Cl in most crystallising mineral phases and (2) the high solubility of Cl in mafic melts. At intermediate-to-silicic compositions, the most important effect is inferred to be the partitioning behaviour of Cl between an exsolving volatile phase and the melt (Webster et al. 2020).

Chlorine enrichment prior to saturation

The relationship between Cl and H2O in magmatic systems is complex and typically displays non-ideal behaviour (Lowenstern 2000; Webster 2004). For very hydrous basaltic melts at relatively deep levels (~51 wt% SiO2, 1105 °C, > 200 MPa, and melt H2O > 5 wt%), experimental data suggest that Cl saturates in the melt at ~2.7 wt% Cl (Webster 2004). Given their low Cl contents and lower H2O contents (~2.5–3 wt. %), we thus infer that the Taupō basalts are Cl-undersaturated. The saturation curve drops by an order of magnitude down to ~0.27 wt% Cl with melt evolution through to rhyolitic compositions and shallower crustal conditions (~75 wt% SiO2, 760 °C, 50 MPa, and melt H2O < 2.7 wt%; Webster 2004, Fig. 10). Chlorine saturation is therefore only expected to occur at evolved rhyolitic compositions in Taupō magmas.

Two minerals present in Taupō magmas do contain Cl: amphibole and apatite. The Cl content of amphiboles in post-Oruanui rhyolites (units B, C, D, E) is ≤ 2000 ppm, less than that of the melt (Barker et al. 2015). As amphibole typically comprises <2 wt% of the crystal cargo and is only considered to be stable in the shallow crystal mush at depths of <250 MPa (Allan et al. 2013), we infer that amphibole crystallisation has only a second-order effect on melt Cl contents (Fig. 3e; Liu et al. 2006; Barker et al. 2015). The Cl contents of Oruanui apatites are ~0.8–1.2 wt%, up to six times higher than the Cl contents of the silicic melts (Online Resource 1). However, apatite occurs only as an accessory mineral in these magmas, and is of insufficient abundance to trigger the observed levels of Cl depletion. Crystallisation of even several wt.% apatite would reduce the melt Cl contents by only a few hundred ppm.

Saturation of a chlorine-rich volatile phase

Fluid/melt partition coefficients for Cl vary from ~10 to ~350 at magmatic conditions, with the highest values corresponding with cooler, lower pressure, silica-rich melts (e.g., Kravchuk and Keppler 1994; Signorelli and Carroll 2000 and references therein; Webster et al. 2009; Doherty et al. 2014). Thus, once the melt becomes saturated, Cl partitions strongly into the exsolving volatile phase relative to the melt (Baker and Alletti 2012 and references therein). The primary control on whether this Cl-rich volatile phase is a Cl-bearing fluid and/or a hypersaline brine phase is the melt H2O/Cl ratio (Webster, 2004, Fig. 10).

The experimental studies of Webster (2004) on granitic compositions at 200 MPa imply that Taupō silicic magmas are at or close to Cl saturation, and will exsolve a Cl-rich vapour phase but not a hypersaline liquid brine (the latter requiring higher Cl/H2O) (Fig. 10). Estimating the depths and compositions at which Taupō magmas begin to exsolve a volatile phase is challenging due to uncertainties in the natural pressure estimates and compositional differences from the experimental starting compositions. Significant scatter in Cl contents occurs in both the melt inclusion and groundmass glass data. However, each magma type shows decreasing Cl contents with increasing SiO2 across all compositions (Fig. 3e), consistent with the presence of a Cl-rich vapour. This inference assumes that the Cl contents of the melt inclusions analysed are representative of the melt with which they last equilibrated during entrapment.

The shallowest regions of the Oruanui melt-dominant magma body are inferred to be in equilibrium with H2O–CO2 fluid at pressures and temperatures less than 200 MPa and 790 °C (Liu et al. 2006; Allan et al. 2017; Myers et al. 2019; Wilson et al. 2021b). These conditions
are below those required for the separation of a single-phase aqueous fluid into separate vapour and brine phases (e.g., Chou 1987). However, Charlier et al. (2012) suggest that the immiscibility curve was not reached until 22 MPa during evacuation of the Oruanui magma. We thus infer that melt Cl contents were fractionated only by a single-phase aqueous fluid, an inference supported by application of the Cl solubility model of Webster et al. (2020). Applying this model to the least and most evolved HSR melt compositions gives Cl solubility maximum (CSM) estimates of 0.59 and 0.56 wt%, respectively, roughly double the recorded Cl contents of the Taupō melts measured here and elsewhere (Dunbar et al. 1989; Hervig et al. 1989; Dunbar and Kyle 1993; Bégué et al. 2015a, 2015b, 2017). Applying the same model to the least and most evolved dacite melt compositions gives CSM estimates of 1.13 and 0.89 wt%, respectively, again much higher than the recorded Cl contents. These results imply that the Taupō magmas were not saturated with a Cl-rich hypersaline brine at any stage.

**Apatite as an indicator mineral for chlorine behaviour**

Chlorine is highly compatible in apatite, which can be used as a tracer for Cl behaviour in magmas (e.g., Zhu and Sverjensky 1991; Mathez and Webster 2005; Webster et al. 2009, 2017; Doherty et al. 2014; Scott et al. 2015; Stock et al. 2018; Humphreys et al. 2021). For example, because Cl partitions strongly into any fluid phase, whereas F prefers the melt, decreasing apatite Cl/F ratios are interpreted to indicate exsolution of an aqueous fluid (e.g., Candela 1986), or alternatively, to reflect decreases in temperature (Piccoli and Candela 2002). Apatite crystals from Taupō magmas show distinctions both between magma types and between orthopyroxene-hosted versus groundmass apatites from the same magma (Fig. 6b). For example, apatites in the Oruanui HSR have distinctly higher XCl / XOH than the other magma types, particularly the LSR. This offset reflects the higher Cl contents in the Oruanui HSR melt as indicated by melt inclusions and groundmass glass (Fig. 3e). The trace-element contents of the apatites are variable, but crystals with higher Cl/F in the HSR typically have lower concentrations of elements that are compatible plagioclase and orthopyroxene (e.g., Sr, Mg, and Mn), consistent with the HSR having undergone additional fractionation of these phases relative to the LSR (Allan et al. 2017; Fig. S2). The higher concentrations of REEs in HSR apatites also reflect crystallisation from a more-evolved, more REE-enriched magma body. Melt H2O contents calculated using apatite Cl contents (Li and Costa 2020) are similar or slightly higher to those measured from melt inclusions averaging 7.1 wt% H2O for HSR, 7.3 wt% for the LSR, 3.7 wt% for the dacites, 9.9 wt% for SG2, and 5.3 wt% for SG3 (Dunbar and Kyle 1993; Liu et al. 2006; Barker et al. 2015; Myers et al. 2019).

Using measured Cl and F contents and the pre-eruptive temperature estimates shown in Fig. 10, we checked for equilibrium between apatite crystals and their host melts (inferred to be represented by melt inclusions for the orthopyroxene-hosted apatites, and groundmass glasses for apatites occurring as free crystals). Apatite-melt exchange coefficients (K_{ap}) for Cl-OH and F-OH were estimated using the ApThermo calculator of Li and Costa (2020). Most orthopyroxene-hosted apatites are close to Cl/F equilibrium with their host melt (where [melt Cl/F calculated from apatite]/[melt Cl/F measured in melt] = 1 ± 0.3: Fig. 6c; Online Resource (1). Notable exceptions are some apatites hosted by orthopyroxene crystals from the dacite magmas, which likely crystallised under hotter conditions in the deeper crust (Barker et al. 2015). However, all groundmass apatite crystals from the Oruanui HSR and LSR are out of equilibrium with the host glass and require either much higher temperatures or 20–30% higher Cl or lower F in the host melt. The groundmass apatites in the HSR have slightly lower XCl / XOH than the orthopyroxene-hosted apatites at elevated XF/ XOH. We interpret these trends to reflect additional late-stage loss of Cl into a pre-eruptive vapour phase as the magmas decompressed during ascent to the surface (e.g., Doherty et al. 2014; McCubbin et al. 2016). In addition, groundmass apatites have higher concentrations of selected trace elements like Na and Li, which could reflect changes fluid salinity or partitioning during decompression (e.g., Charlier et al. 2012; Fig. S2). Similar observations were made by Humphreys et al. (2021) for the Laacher See deposits, where disequilibrium between apatites and their host melt were inferred to reflect reorganisation of crystal mush and partitioning of Cl into a vapour phase prior to eruption. Timescale estimates for diffusive equilibration shown in Table 2 of Humphreys et al. (2021) (after Brenan 1993) indicate that groundmass apatite crystals of 22.5 µm size would take ~5 days to re-equilibrate with their host melt at temperatures appropriate for the Oruanui rhyolites (~800 °C). Notably, these timescales merge with those estimated for the onset of initial slow magma ascent as inferred from diffusive loss of hydrogen in Oruanui melt inclusions (1–5 days: Myers et al. 2019). These findings highlight the potential use of apatite to provide insights into the pre-eruptive exsolution of halogens and the timescales leading to final eruption.

**Summary of chlorine evolution below Taupō volcano**

The inferred transport of Cl during magmatic evolution beneath Taupō is shown in Fig. 11. The relatively low Cl contents of the basaltic melt inclusions reflect those of the primitive feedstock magmas. The enrichment in Cl in the silicic melts relative to the basalts is inferred to reflect the net incompatibility of Cl (i.e., bulk K_{ap} < 1) during extensive crystallisation-driven differentiation (point 1 in Fig. 11).
Subsequently, the onset of apatite and/or amphibole crystalisation reduces the amount of Cl available in the melt and slows the rate of Cl enrichment (point 2). As melt evolution progresses with further crystallisation, the fluid/melt partition coefficient for Cl increases steadily. After extensive crystal fractionation and at shallow levels (< 200 MPa), the magma becomes volatile saturated and a Cl-bearing fluid exsolves, leading to depletion of Cl in the melt (point 3). Decreasing glass Cl contents and lowering of $X_{\text{Cl}}/X_{\text{OH}}$ in the Oruanui HSR groundmass apatites relative to those hosted by orthopyroxene are inferred to reflect loss of Cl to this fluid. Disequilibrium in Cl/F between groundmass apatites and their host rhyolite glass implies pre-eruptive Cl loss from the melt shortly before eruption, as noted for other large rhyolite eruptions and further discussed below.

**Behaviour of fluorine**

The behaviour of F in Taupō magmas is challenging to interpret, because the basaltic and silicic melt inclusions have similar F contents. However, several factors are relevant: (1) the high solubilities of F in silicate melts at magmatic conditions; (2) the high compatibility of F in amphibole and apatite and the timing of their crystallisation; and (3) the destabilisation of amphibole at a late stage in the Oruanui HSR magma (Allan et al. 2013).

Fluorine is highly soluble in silicate melts and it is uncommon for them to reach F saturation (London et al. 1988; Piccoli and Candela 2002; Mathez and Webster 2005; Dolejš and Baker 2007; Aiuppa et al. 2009; Webster et al. 2009, 2017; Doherty et al. 2014). Fluorine also partitions in favour of melt relative to aqueous fluid until melt F concentrations exceed several weight percent (e.g., Webster 1990; Webster and Holloway 1990; Dolejš and Baker 2007), and is incompatible in most major mineral phases. In basaltic magmas, F is expected to be progressively enriched in the melt during fractionation, but in intermediate composition melts, the crystallisation of F-compatible phases (apatite and/or amphibole) may affect this trend.

**Apatite as an indicator mineral for fluorine behaviour**

Because F (like Cl) preferentially partitions into apatite relative to silicic melt, apatite is a useful tracer for F behaviour during crystallisation (Candela 1986; Piccoli and Candela 2002; Mathez and Webster 2005; Webster et al. 2009, 2017; Marks et al. 2012; Doherty et al. 2014; Scott et al. 2015). However, F prefers to stay in the melt rather than partition into any fluid phase. The trace-element composition of apatites reflects the degree of magma evolution where the HSR apatites have lower concentrations of compatible elements when compared to the LSR (Fig. S2). Enrichment of $X_{\text{F}}/X_{\text{OH}}$ in apatite can also be considered to reflect evolution of magma, as highlighted by the elevated $X_{\text{F}}/X_{\text{OH}}$ in the LSR groundmass apatites when compared to the orthopyroxene-hosted apatites (Fig. 6b). However, the Oruanui HSR apatites have lower or comparable $X_{\text{F}}/X_{\text{OH}}$ than the LSR and the other magma types (Fig. 6b). Offsets in apatite compositions and melt F content (Fig. 3f) is likely due to the extensive crystallisation of amphibole in the shallow Oruanui HSR magma body (Allan et al. 2013). Amphibole can incorporate F to up to wt% levels (e.g., Ekstrom 1972; Chambefort et al. 2013; Van den Bleeken and Koga 2015) and partitioning of F into amphibole reduces the amount available in the melt for apatite. In turn, late-stage breakdown of amphibole could also liberate F back into the melt and increase the $X_{\text{F}}/X_{\text{OH}}$ in the apatite. The generally higher values and wide scatter in F contents of several HSR groundmass glasses with SiO$_2$ > 77 wt% (Fig. 3f) may reflect in part the release of F back into the melt via amphibole resorption (Allan et al. 2013, 2017).

**Summary of fluorine transport below Taupō volcano**

Discerning the dominant controls on F transport below Taupō volcano is challenging, because the data show no convincing trends. A tentative magmatic pathway (Fig. 12) shows increasing F values relative to SiO$_2$ in the basaltic melts due to the fractional crystallisation of F-free minerals (point 1). If apatite begins to crystallise, F levels decrease with SiO$_2$ (point 2). In the amphibole-free (post-Oruanui) magmas, apatite is the only major F-bearing phase...
et al. 2013, 2017), but could also be indicative of an increase in F abundances in some Oruanui HSR melt compositions (Fig. 3) may represent amphibole breakdown in the most evolved HSR melts (Allan et al. 2013, 2017), but could also be indicative of an increasing compatibility of F in the melt (point 3).

Estimating sulfur and halogen emissions from past explosive eruptions

Large explosive volcanic eruptions have profound impacts on the environment and climate as ash, aerosols, and gases are injected into the atmosphere (Rampino et al. 1988; Sigl et al. 2015). Outgassed S species (e.g., SO2) are readily oxidised to form sulfate aerosols (SO4\(^{2-}\)) that effectively scatter incoming shortwave solar radiation and can remain suspended for long periods in the stratosphere, triggering global or hemispheric cooling (Langmann 2014; Osipov et al. 2021). For example, the release of S during the 1991 Pinatubo eruption (~ 10 km\(^3\) ash) reduced average global temperatures by ~0.5 °C in the following year (McCormick et al. 1995). Halogen emissions from eruptions can also impact on atmospheric chemistry, with Cl reactions in the stratosphere leading to ozone depletion (Textor et al. 2003; von Glasow et al. 2009; Krüger et al. 2015; Waelkens et al. 2009). By comparing melt inclusion and groundmass glass S contents for the 1.8 ka Taupō and Oruanui eruptions, we calculate petrological estimates of ~1.9 and 8.5 Tg S release (for 35 and 530 km\(^3\) magma), respectively (Table 2). These values are too low when compared with the ice core records (Sigl et al. 2013; Dunbar et al. 2017; Lin et al. 2022). Such disparities are common when comparing petrological estimates of S emissions with those measured from other techniques, such as remote sensing, satellite observations, or ice core records (Devine et al. 1984; Wallace 2001). Among possible explanations is the presence of a separate fluid phase that exsolved from the magma before melt-inclusion entrapment (e.g., Westrich and Gerlach 1992; Wallace 2001). Indeed, our results suggest that exsolution of an aqueous fluid phase was a key driver of S depletion of the melt (to a minimum of <60 ppm). Scaillet and Pichavant (2003) used a thermodynamic approach to estimate partitioning of S (D\(_S\)gas/melt) from the melt to a fluid (gas) phase for several eruptions (including the Unit Y/Taupō eruption) and developed a method that accounted for S in the exsolving gas phase at depth in addition to the S dissolved in the melt. Geochemical modelling, remote-sensing data, experimental constraints, and the presence of vapour bubbles in melt inclusions indicate that up to 6 wt% gas may separate out in the upper reaches of silicic magma reservoirs prior to eruption (Wallace 2001; Scaillet et al. 2003). Assuming

\[ F_{\text{ppm}} = \frac{F_{\text{total}}}{1000} \]

\[ S_{\text{total}} = S_{\text{analyzed}} + S_{\text{inclusion}} \]

\[ D_{S}\text{gas/melt} = \left( \frac{P_{\text{melt}}}{P_{\text{gas}}} \right) D_{S}\text{melt/liquid} \]

\[ P_{\text{melt}} = \frac{P_{\text{total}}}{1000} \]

\[ P_{\text{gas}} = \frac{P_{\text{total}}}{1000} \]

\[ D_{S}\text{melt/liquid} = \frac{S_{\text{melt}}}{S_{\text{liquid}}} \]

\[ S_{\text{melt}} = S_{\text{analyzed}} + S_{\text{inclusion}} \]

\[ S_{\text{liquid}} = S_{\text{analyzed}} \]

\[ P_{\text{total}} = P_{\text{melt}} + P_{\text{gas}} \]

\[ S_{\text{analyzed}} + S_{\text{inclusion}} = S_{\text{total}} \]

\[ D_{S}\text{gas/melt} = \left( \frac{S_{\text{analyzed}}}{S_{\text{total}}} \right) D_{S}\text{melt/liquid} \]

\[ D_{S}\text{gas/melt} = \left( \frac{S_{\text{analyzed}}}{S_{\text{total}}} \right) \left( \frac{P_{\text{melt}}}{P_{\text{gas}}} \right) \]

\[ D_{S}\text{gas/melt} = \left( \frac{P_{\text{melt}}}{P_{\text{gas}}} \right) \left( \frac{S_{\text{analyzed}}}{S_{\text{total}}} \right) D_{S}\text{melt/liquid} \]

\[ D_{S}\text{gas/melt} = \left( \frac{P_{\text{melt}}}{P_{\text{gas}}} \right) \left( \frac{S_{\text{analyzed}}}{S_{\text{total}}} \right) \left( \frac{S_{\text{melt}}}{S_{\text{liquid}}} \right) \]

\[ D_{S}\text{gas/melt} = \left( \frac{P_{\text{melt}}}{P_{\text{gas}}} \right) \left( \frac{S_{\text{analyzed}}}{S_{\text{total}}} \right) \left( \frac{S_{\text{melt}}}{S_{\text{liquid}}} \right) \]

\[ D_{S}\text{gas/melt} = \left( \frac{P_{\text{melt}}}{P_{\text{gas}}} \right) \left( \frac{S_{\text{analyzed}}}{S_{\text{total}}} \right) \left( \frac{S_{\text{melt}}}{S_{\text{liquid}}} \right) \]

\[ D_{S}\text{gas/melt} = \left( \frac{P_{\text{melt}}}{P_{\text{gas}}} \right) \left( \frac{S_{\text{analyzed}}}{S_{\text{total}}} \right) \left( \frac{S_{\text{melt}}}{S_{\text{liquid}}} \right) \]
gas S contents for the Unit Y/Taupō eruption of ~1200 ppm (after Scaillet and Pichavant 2003) and slightly higher values for the Oruanui HSR (2000 ppm) (Keppler 2010), we calculate considerably higher S releases of ~6.7 Tg and 130.4 Tg, respectively, using the method of Scaillet et al. (2003) (Table 2). Assuming that all of the S released in these events was converted to sulfate, our revised calculations are highly comparable to the bi-polar ice core estimates of S loading associated with these events (Gao et al. 2007; Sigl et al. 2013; Lin et al. 2022; Table 2). These calculations are, however, subject to significant uncertainties (Scaillet et al. 2003) such as the pre-eruptive gas content and the amount of S scavenging by adsorption onto ash particle surfaces in the eruption cloud (e.g., Taylor and Stoiber 1973; Rose 1977; Rose et al. 1982; Varekamp et al. 1984).

Two additional sources may contribute to eruptive S budgets at Taupō. First, up to 5 km³ of S-rich mafic magma may have recharged the magmatic system prior to the Unit Y (Taupō) eruption (Barker et al. 2016) and 3–5 km³ of mafic magma was co-erupted with rhyolite in the Oruanui event (Wilson 2001; Wilson et al. 2006; Allan et al. 2017; Rooyakkers et al. 2018). Assuming $K_D(S)_{gas/melt} \approx 10$ and a gas content of 1 wt. %, some tens of Tg of additional S could have been contributed from mafic recharge and/or discharge (Table 2). Second, caldera-forming eruptions will release any S sequestered in the hydrothermal envelope surrounding the magma system, although in the Taupō context, no quantitative estimates can be made of the S contribution from this source.

Halogen contents are substantially higher than S contents in the Taupō silicic magmas but estimating their emissions during past eruptions is challenging. Due to the slow diffusion of halogens in rhyolitic melts compared to other volatiles such as H₂O (e.g., Schipper et al. 2019; Waelkens et al. 2021), syn-eruptive degassing of silicic melts during final ascent and vesiculation is not considered to be a significant source of halogen emissions in explosive events. The post-Oruanui dacites are the only samples where halogens are depleted in the groundmass glass relative to melt inclusions (Fig. 3e, f), perhaps reflecting their deeper storage conditions (>200 MPa: Barker et al. 2015) which may have allowed greater time for halogen degassing during ascent. Despite the lack of significant syn-eruptive Cl exsolution from the rhyolites, our study indicates that significant amounts of Cl were lost from these melts into a pre-eruptive fluid phase (Fig. 11), which could have been a significant source of Cl emissions during eruption (e.g., Humphreys et al. 2021).

The partitioning of Cl from the melt to fluids depends on several factors, including pressure, temperature, CO₂ concentrations, and fluid salinity (Hsu et al. 2019). CO₂ concentrations in Taupō rhyolite melts are typically low (<200 ppm measured in sealed melt inclusions: Myers et al. 2019) and previous pressure and temperature estimates of rhyolite

### Table 2: Sulfur flux calculations from past eruptions of Taupō volcano, compared to ice core estimates

| Eruption | Volume (km³) | S in melt (ppm) | S in groundmass (ppm) | S in pre-eruptive fluid (ppm) | Mass magma (Tg) | Mass S in melt (Tg) | Mass S in gas (Tg) | Total mass S (Tg) | Global sulfate loading (Tg) |
|----------|--------------|----------------|----------------------|-----------------------------|----------------|-------------------|------------------|----------------|-----------------|
| Taupō 1.8 ka | 35           | 50             | 27                   | 1200                        | 80,500         | 1.9                | 1.9               | 2.8            | 14 ± 4.3         |
| Oruanui HSR | 530         | 33             | 26                   | 2000                        | 1,219,000      | 8.5                | 8.5               | 17             | ~200            |
| Taupō basalt | 5           | 1500           | n/a                  | 15,000                      | 13,500         | 20.3               | 20.3              | 40.6           | ~382            |

Calculations based on the improved petrological method of Scaillet et al. (2003). Mass S in melt (Smelt) is the amount of S released using the difference between average S content of melt inclusions (S in melt) and S content of groundmass glass (S in groundmass). The mass of gas (S in gas) is calculated using the amount of S in the pre-eruptive fluid phase (S in pre-eruptive fluid) using 1200 ppm for Taupō 1.8 ka (Scaillet and Pichavant 2003), 2000 ppm for Oruanui (Keppler 2010) and 1500 ppm for basalt (Scaillet et al. 2003), multiplied by the mass of the erupted magma and assuming a gas content of 1 wt. % for rhyolite and 5 wt. % for basalt, respectively. The mass of the erupted magma is from Wilson (1993, 2001) and Allan et al. (2017), and Barker et al. (2016). Global sulfate loading values are from Sigl et al. (2013) for Taupō 1.8 ka and Lin et al. (2022) using the methods of Gao et al. (2007).
magma storage at Taupō provide a basis for estimating the Cl content of a vapour phase (Table 3; Barker et al. 2015; Allan et al. 2017). Fluid-melt partition coefficients for Cl ($K_D(\text{Cl})_{\text{fluid/melt}}$), however, are highly sensitive to pressure, such that small changes over the pressure ranges estimated at Taupō based on melt-inclusion studies (Myers et al. 2018, 2019), mineral barometry (Barker et al. 2015; Allan et al. 2017), and rhyolite-MELTS (Bégué et al. 2014) result in order of magnitude changes to the calculated $K_D$.

The upper range of the calculated Oruanui Cl flux is lower than that estimated for the lower Bandelier Tuff (~4800 Tg: Waelkens et al. 2021), but broadly similar to that estimated for the ~84 ka Los Chocoyos eruption (~ 1200 Tg: Brenna et al. 2019). Fluxes from these supereruptions greatly exceed those calculated for smaller explosive eruptions including the Minoan eruption of Santorini (~675 Tg: Cadoux et al. 2015), the 1257 Samalas eruption (227 Tg: Vidal et al. 2016), the Laacher See eruption (~32 Tg: Humphreys et al. 2021), or the two largest-emitting eruptions in the modern era, El Chichón and Pinatubo (approximately 1.8 and 3–4.5 Tg of chlorine, respectively: Varekamp et al. 1984; Self et al. 1996). The Cl flux calculated for the smaller volume 1.8 ka Taupō event is much lower at ~45 Tg. However, these estimates do not account for possible halogen outgassing over long periods during effusive activity, such as during the 2011–2012 Cordón Caulle eruption where >90% of the 6.3 Tg of HCl and >98% of the 1.9 Tg of HF was released after explosive activity ended (Schipper et al. 2019). As for S flux estimates, halogen calculations are subject to many uncertainties and further work is required to refine the environmental and climatic impacts of these events.

**Conclusions**

We have quantified the concentration and behaviour of S, Cl, and F in the magmas of Taupō volcano using mafic and silicic melt inclusions and apatite crystals. We show that the principle controls on the transport pathways and abundances of S, Cl, and F differ for each element. Concentrations of all three elements initially increase in mafic magmas as they evolve by crystallisation, but subsequently diverge due to a variety of processes. A schematic model is presented in Fig. 13 and the key stages of magma evolution controlling S and halogen behaviour in the large magmatic system beneath Taupō volcano are as follows:

1. **Fractional crystallisation of primitive melts.** Olivine and pyroxene fractionation is inferred to be the main control on the abundances and behaviour of incompatible S, Cl, and F in the primitive basaltic melts as measured in melt inclusions from high-Mg olivines. No melts are volatile saturated at this early stage in the deep system.

2. **Sulfur saturation.** Sulfur contents initially increase with differentiation due to the incompatibility of S during early crystallisation. Sulfur saturation is eventually reached at intermediate melt compositions, triggered by a decrease in $f_O^2$ upon the onset of magnetite crystallisation (the ‘magnetite crisis’). This leads to the crystallisation of pyrrhotite.

3. **Crystallisation of magnetite, pyrrhotite, apatite, and amphibole.** The exact order in which these minerals crystallise is not fully constrained, but the ‘magnetite crisis’ likely also triggers apatite crystallisation. Additional effects include further decreases in $f_O^2$, which convert the majority of sulfate present in the melt to sulfide and lower the S saturation threshold. Continuing

**Table 3 Chlorine flux calculations from past eruptions of Taupō volcano**

| Eruption   | Volume (km$^3$ DRE) | Mass magma (Tg) | Magma temp (°C) | Storage P (MPa) | Cl$_{\text{MELT}}$ (ppm) | XCO$_2$ | $K_D(\text{Cl})_{\text{fluid/melt}}$ | Cl$_{\text{fluid}}$ (ppm) | Mass Cl$_{\text{fluid}}$ erupted (Tg) |
|------------|---------------------|-----------------|-----------------|-----------------|--------------------------|---------|-------------------------------|---------------------------|-------------------------------|
| Taupō 1.8 ka | 35                  | 80,500          | 850             | 200             | 1900                     | 0.16    | 14.7                          | 27,996                    | 45                            |
|            |                     |                 |                 | 150             | 1900                     | 0.16    | 6.4                           | 12,127                    | 20                            |
|            |                     |                 |                 | 100             | 1900                     | 0.16    | 2.7                           | 5164                      | 8                             |
| Oruanui HSR | 530                 | 1,219,000       | 790             | 200             | 2035                     | 0.1     | 35.7                          | 72,746                    | 1774                          |
|            |                     |                 |                 | 150             | 2035                     | 0.1     | 10.6                          | 21,547                    | 525                           |
|            |                     |                 |                 | 100             | 2035                     | 0.1     | 3.8                           | 7803                      | 190                           |

Magma volumes and masses as in Table 3, magma temperatures are from Barker et al. (2015) and Allan et al. (2017). $K_D(\text{Cl})_{\text{fluid/melt}}$ calculated using Eq. 6 from Hsu et al. (2021), where XCO$_2$ is the molar fraction of CO$_2$ in the fluid, calculated using H$_2$O–CO$_2$ mixed fluid saturation model for rhyolite-MELTS from Ghiorso and Gualda (2015) using average glass compositions from this study and 4.5 wt% H$_2$O for Taupō 1.8 ka, 5.5 wt% H$_2$O for Oruanui and 200 ppm CO$_2$ for both magma types (Dunbar and Kyle, 1993; Myers et al. 2018). Mass of erupted Cl calculated by multiplying the concentration of Cl in the pre-eruptive fluid phase by the mass of fluid exsolved from the pre-eruptive magma as estimated by the loss of ~2 wt. % H$_2$O between melt inclusions and re-entrants in the Oruanui HSR (from Myers et al. 2019).
pyrrhotite crystallisation depletes S in the melt down to low values, while apatite crystallisation (along with amphibole, if present) also depletes the melt of F.

4. **Aqueous fluid saturation.** Volatile contents required for H₂O and CO₂ fluid saturation may occur at pressures sampled by the deepest Oruanui LSR and post-Oruanui dacites (> 200 MPa, 900–950 °C) and are ubiquitous at shallower depths (Liu et al. 2006; Myers et al. 2019), such that an aqueous fluid exsolves from the melt. The fluid phase strongly fractionates S, preventing further pyrrhotite crystallisation and buffering melt S contents at minimal values (< 150 ppm) for the remainder of the differentiation pathway (as sampled by silicic melt inclusions). At similar depths, the melt reaches saturation with a Cl-rich vapour which is sequestered into the aqueous fluid phase and may be transferred into the enclosing hydrothermal system.

5. **Amphibole pause/resorption.** Amphibole becomes unstable in the most evolved melts at SiO₂ > 76 wt%, causing a reversal of the F depletion trend as amphibole breaks down and releases F back into the melt (Allan et al. 2013).

6. **Volatile exsolution at the onset of magma rise.** Immediately prior to eruption, initial slow decompression at the beginning of magma rise (Myers et al., 2019) leads to further exsolution of volatiles and additional loss of S and Cl from the melt to the fluid phase. This late-stage Cl loss is reflected by disequilibrium halogen partitioning between apatite crystals and their host melts, which is inferred to reflect further loss of Cl to a pre-eruptive vapour within a few days of eruption.

7. **S and halogen flux from past eruptions.** S and halogen emissions from past explosive eruptions from Taupō were dominantly sourced from gas and/or fluid phases. This accounts for the substantial sulfate anomalies attributed to the Taupō and Oruanui eruptions from the ice core record, despite the low S contents of their rhyolite glass and melt inclusions. Additional S and halogens from these explosive eruptions may have also been contributed by mafic recharge magmas and/or destruction of the hydrothermal envelope during caldera collapse. The Oruanui supereruption was one of the largest S-producing explosive eruptions in the ice core record and also ejected huge masses of Cl, which would have led...
to significant volcanogenic cooling and ozone depletion on a global scale.

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