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Abstract

Hydrothermal alteration is considered to increase the likelihood of dome or flank collapse by compromising stability. Understanding how such alteration influences rock properties, and providing independent metrics for alteration that can be used to estimate these parameters, is therefore important to better assess volcanic hazards and mitigate risk. We explore the possibility of using whole-rock $\delta^{18}O$ and δD values and water contents, metrics that can potentially track alteration, to estimate the strength (compressive and tensile) and Young's modulus (i.e. "stiffness") of altered (acid-sulfate) volcanic rocks from La Soufrière de Guadeloupe (Eastern Caribbean). The $\delta^{18}O$ values range from 5.8 to 13.2‰, δD values from –151 to –44‰, and water content from 0.3 to 5.1 wt%. We find that there is a good correlation between $\delta^{18}O$ values and laboratory-measured strength and Young's modulus, but that these parameters do not vary systematically with δD or water content (likely due to their pre-treatment at 200 °C). Empirical linear relationships that allow strength and Young's modulus to be estimated using $\delta^{18}O$ values are provided using our new data and published data for Merapi volcano (Indonesia). Our study highlights that $\delta^{18}O$ values can be used to estimate the strength and Young's modulus of volcanic rocks, and could therefore be used to provide parameters for volcano stability modelling. One advantage of this technique is that $\delta^{18}O$ only requires a small amount of material, and can therefore provide rock property estimates in scenarios where material is limited, such as borehole cuttings or when sampling large blocks is impracticable.

Keywords: La Soufrière de Guadeloupe; Merapi; porosity; uniaxial compressive strength; tensile strength; Young's modulus; whole-rock oxygen isotope ratio

Résumé

L'altération hydrothermale est considérée comme l'un des principaux facteurs augmentant les risques d'effondrement du dôme ou des flancs d'un volcan et ainsi de compromettre sa stabilité. Il est donc fondamental de comprendre comment l'altération influence les propriétés physiques des roches et d'identifier des marqueurs permettant de la quantifier en même temps que les paramètres physiques les plus importants. Le but est de mieux analyser la dynamique d'un édifice volcanique et de limiter les risques. Nous avons exploré l'utilisation des mesures isotopiques $\delta^{18}O$ et δD et de la teneur en eau sur un volume de roche, mesures qui potentiellement permettent de suivre l'altération (principalement par acide à sulfates), de quantifier la résistance mécanique (en tension et en compression) et le module d'Young de roches altérées provenant de La Soufrière de Guadeloupe.

Les valeurs de $\delta^{18}O$ varient entre 5.8 et 13.2‰, alors celles de δD sont comprises entre 151 to –44‰, et la teneur en eau entre 0.3 to 5.1 wt%. Il y a une très bonne corrélation entre les valeurs de $\delta^{18}O$ et la résistance mécanique et les paramètres élastiques des roches mesurés en laboratoire. Ces paramètres ne varient cependant pas de façon systématique avec les valeurs de δD et la teneur en eau. La compilation de données publiées sur le volcan de Merapi (Indonésie) avec nos nouveaux résultats, montre que la résistance mécanique et le module d'Young peuvent être estimés empiriquement à l'aide d'une simple relation linéaire en fonction des valeurs de $\delta^{18}O$. Notre étude suggère par conséquent que le $\delta^{18}O$ peut être utilisé comme paramètre de bases des modèles de stabilités des édifices volcaniques. L'avantage principal réside dans le fait que les mesures de $\delta^{18}O$ ne nécessitent qu'une très petite quantité de roches et pourront donc permettre d'estimer les propriétés physiques des roches dans des situations où les quantités de matériau accessible sont faibles, notamment quand le prélèvement de larges blocs est impossible (typiquement à partir des cuttings de forages).

1 Introduction

Geophysical techniques have revealed large subsurface hydrothermal systems within active volcanoes worldwide (Aizawa et al., 2009; Finizola et al., 2010; Troll et al., 2012; Rosas-Carbajal et al., 2016; Byrdina et al., 2017, 2018; Ghorbani et al., 2018; Finn et al., 2018; Ahmed et al., 2018; Tseng et al., 2020; Kereszturi et al., 2021; Finn et al., 2022). The hydrothermal fluids circulating within these systems can physically and chemically alter the rocks (Browne, 1978), which is thought to increase the likelihood of potentially devastating dome or partial edifice flank collapse by compromising their stability (Day, 1996; van Wyk de Vries et al., 2000; Reid et al., 2001; Voight et al., 2002; Reid, 2004; Cecchi et al., 2004; Salaün et al., 2011; Ball et al., 2015, Rosas-Carbajal et al., 2016; Ball et al., 2018; Mordensky et al., 2019; Heap et al., 2021a, b; Harnett and Heap, 2021; Darmawan et al., 2022; Mordensky et al., 2022). Dome or edifice collapse can suddenly decompress pressurised hydrothermal systems or gas-rich magma present at shallow depth hence triggering the formation of devastating highly mobile high-energy pyroclastic density currents (blasts) exemplified by the classic 1980 eruption of Mount St. Helens (USA) as well as other eruptions of varying magnitudes (Lipman and Mullineaux, 1981; Voight et al., 1981; Hoblitt et al., 1981; Sparks et al., 2002; Voight et al., 2002; Boudon et al., 2005; Belousov et al., 2007; Lube et al., 2012; Komorowski et al., 2013). As a result, the monitoring of hydrothermal alteration at active volcanoes, and understanding how alteration influences rock physical and mechanical properties, are important to better assess volcanic hazards and mitigate risk.

Previous experimental studies have shown that hydrothermal alteration can decrease (del Potro and Hürlimann, 2009; Frolova et al., 2014; Wyering et al., 2014; Mayer et al., 2016; Farquharson et al., 2019; Heap et al., 2020a, 2021a; Darmawan et al., 2022; Heap et al., 2022a) or increase (Marmoni et al., 2017; Heap et al., 2020a, b, 2021b) the strength and Young's modulus of volcanic rocks. Whether alteration decreases or increases strength or Young's modulus is thought to depend on (1) whether the alteration increases or decreases the porosity of the rock, a factor known to exert a first-order control on the strength and Young's modulus of volcanic rocks and (2) whether the alteration minerals are weaker/softer or stronger/stiffer than the primary mineral assemblage (Heap et al., 2020a; Heap and Violay, 2021; Darmawan et al., 2022). Heap et al. (2021b) recently suggested that both porosity-increasing and porosity-decreasing alteration could jeopardise volcano stability. These authors argued that porosity-increasing alteration affects volcano stability by reducing rock strength and stiffness, whereas porosity-decreasing alteration reduces permeability and increases pore fluid pressure (Heap et al., 2021b).

A step change in volcano hazard monitoring is possible if rock physical and mechanical properties can be accurately estimated using an independent metric that quantifies alteration. Recently, Heap et al. (2021a, 2022a) showed that the strength (compressive and tensile) and Young's modulus of variably altered rocks from La Soufrière de Guadeloupe (Eastern Caribbean) can be estimated using the amount of alteration minerals in wt%, quantified using X-ray powder diffraction (XRPD) data. Using Mt. Ruapehu (New Zealand) as a case study, Schaefer et al. (2021) showed that it is possible to estimate the physical and mechanical properties of volcanic rocks using rapid, non-invasive reflectance spectroscopy measurements. More recently, Darmawan et al. (2022) found that the compressive strength of variably altered rocks from Merapi volcano (Indonesia) can be estimated using whole-rock $\delta^{18}O$ values.

Whole-rock $\delta^{18}O$ values can serve as an indicator for alteration because hydrothermal processes often entail an exchange of oxygen isotopes between solid igneous mineral phases and circulating fluids, or the formation of new minerals such as clay minerals or sulfates (Taylor, 1974; Hansteen and Troll, 2003; Donoghue et al., 2008; Berg et al., 2018). We highlight that magmatic variations in $\delta^{18}O$ values are typically small and pristine igneous rocks usually have $\delta^{18}O$ ratios between 5 and 8‰ (Taylor 1974; Bindeman, 2008; Deegan et al., 2021). Indeed, variations due to closed-system fractional crystallisation are usually <1‰ (Bindeman, 2008). Whole-rock $\delta^{18}O$ values generally increase in volcanic rocks as a function of relatively low temperature hydrothermal alteration ($\leq$ 250 °C), whereas higher temperatures ($\geq$ 400 °C) or isotopically very light meteoric waters usually tend to decrease the $\delta^{18}O$ of the mineral assemblage (Taylor, 1974; Rose et al., 1994; Donoghue et al., 2010; Darmawan et al., 2022). Here, we further explore the relationship between whole-rock $\delta^{18}O$ values, as well as δD values and water

contents, and the strength (compressive and tensile) and Young's modulus of hydrothermally altered volcanic rocks. The goal of this contribution is to test whether isotopic compositions and water contents of hydrothermally altered (acid-sulfate) volcanic rocks can be used to estimate their physical and mechanical properties.

2 Materials and Methods

A suite of 19 variably altered rocks from La Soufrière de Guadeloupe, an active andesitic stratovolcano located on the French island of Guadeloupe in the Eastern Caribbean (Komorowski et al., 2005; Moretti et al., 2020), were used for this study (sampling locations are shown in Fig. 1).

Volcanic unrest at La Soufrière de Guadeloupe has increased since its reawakening in 1992. This unrest is manifest as the expansion of the hot outgassing area at the top of the current lava dome (which formed in CE 1530), the appearance of steam-dominated fumaroles and acid chloride-sulfate springs, an increase in summit and flank displacement rates, an increase in the heat output from the dome, an abundance of shallow seismicity, and, in April 2018, the largest felt tectonic earthquake since the last eruption in 1976–1977 (Brombach et al., 2000; Villemant et al., 2005, 2014; Moretti et al., 2020; Jessop et al., 2021; Heap et al., 2021a; Moune et al., 2022). The link between the stability of the volcano and a combination of hydrothermal alteration resulting from hydrothermal circulation and chemical weathering due to the tropical environment has been underscored in several contributions (Komorowski et al., 2005; Le Friant et al., 2006; Salaün et al., 2011, Rosas-Carbajal et al., 2016; Peruzzetto et al., 2019; Heap et al., 2021a; Moretti et al., 2021; Metcalfe et al., 2021; Moune et al., 2022). As a result, La Soufrière de Guadeloupe represents an ideal natural laboratory to study the influence of hydrothermal alteration on rock physical and mechanical properties and volcano stability.

Indeed, La Soufrière of Guadeloupe is characterised by an exceptional recurrence of partial edifice collapse with at least nine flank collapses that have occurred in the last 9150 years, the last of which occurred during the 1530 CE eruption (Komorowski et al., 2005; Boudon et al., 2007; Komorowski et al., 2012; Legendre, 2012; Peruzzetto et al., 2019). Evidence from the geological record indicates that the frequency of partial edifice collapse in the last 9150 years has increased compared to older eruptive episodes of the Grande Découverte volcanic complex, although the collapse volume has decreased. Finally, there is a high probability that edifice collapse will trigger laterally-directed explosions (between two and five of the eight edifice collapses of the last 8500 years generated laterally-directed blasts) (Komorowski et al., 2005; Boudon et al., 2007; Komorowski et al., 2012; Legendre, 2012; Peruzzetto et al., 2019).

All of the 19 blocks analysed in this study are sourced from either coherent lava blocks or coherent lavas (i.e. we did not collect blocks of, for example, breccia). Of the 19 blocks collected, nine were collected from a collapse scar to the northeast of dome summit (blocks H2A, H2B, H3, H4A, H5A, H6, H25, H29, and H30). Five blocks were collected from the dome summit: four blocks were collected from the lava spines that protrude the dome (two blocks from Cratère Sud Central, H19 and H20, and two blocks from an adjacent site, H21 and H22), and one block was collected from the wall of the Lacroix Supérieur outgassing fracture on the lava dome (H18). A block was collected to the southwest of dome summit from a collapse scar into a highly fractured lava that forms the core of a paleo-collapse mega-block of the former volcanic edifice (WP1285). Blocks were also collected from the West wall of the fault "Faille 30 août" on the lava dome (H14 and H15), and from a thick lava adjacent to the Galion waterfall not associated with the CE 1530 dome (H32). The final block, a volcanic non-juvenile bomb from the dome that was ejected during the 1976–1977 explosive eruption (Komorowski et al., 2005), was taken from the roof of a small disused thermal bathhouse to the South of the dome summit (WP1317).

These rocks, previously described by Heap et al. (2021a, 2022a, b), are andesites characterised by a porphyritic texture comprising magmatic phenocrysts of dominantly plagioclase and pyroxene (orthopyroxene and clinopyroxene) within a microcrystalline groundmass. The mineral assemblage present in each block was identified by a combination of optical microscopy, Raman spectroscopy, and X-ray powder diffraction (XRPD), and quantitative phase analysis was performed using the XRPD data and Rietveld program BGMN (Bergmann et al., 1998) (for more details see Heap et al., 2021a, 2022a, b). The XRPD data show that all of the rocks contain variable quantities of secondary (alteration) minerals: kaolinite, alunite or natro-alunite, silica polymorphs (quartz, cristobalite, tridymite, and opal-A), hematite, pyrite, gypsum, and talc (Heap et al. 2021a, 2022a, b; Table 1). The predominant hydrous alteration phases are kaolinite, natro-alunite, and opal-A in these materials (Table 1) suggesting fluid-rock interaction with acidic sulfate-chloride-rich fluids at relatively low temperatures (< 150–200 °C) (Inoue, 1995; Zimbelman et al., 2005; Scher et al., 2013; Fulignati, 2020; Heap et al., 2021a). Indeed, theses rocks do not contain smectite, which is not stable in highly acidic (low pH) environments. High-temperature acidic alteration minerals, such a pyrophyllite, dickite, diaspore, zunyite, or topaz, are notably absent, and talc was observed in only one sample (H22) in relatively low amounts (Table 1). The alteration intensity of the 19 blocks from La Soufrière de Guadeloupe has been quantified in previous contributions by the weight percentage (wt%) of secondary (i.e. alteration) minerals (Heap et al., 2021a, 2022a, b) and these data are available in Table 2.

In this contribution, we relate new whole-rock oxygen and hydrogen isotope ratio data, and H_2O concentrations, with previously published data for the physical and mechanical properties of rocks from La

Soufrière de Guadeloupe. The uniaxial compressive strength (UCS), indirect tensile strength (ITS), and Young's modulus values for multiple cylindrical samples prepared from the blocks collected from La Soufrière de Guadeloupe were published in previous contributions by Heap et al. (2021a, 2022a). UCS was measured on oven-dry cylindrical samples in a uniaxial load frame using a constant axial strain rate of 10^{-5} s^{-1} (Heap et al., 2021a). Young's modulus, an elastic constant that describes the "stiffness" of a material, was then calculated from the pseudo-linear elastic portion of the resultant uniaxial stress-strain curves (Heap et al., 2021a). ITS was measured on oven-dry discs, deformed diametrically in compression using a uniaxial load frame and a constant displacement rate of 0.025 mm. s^{-1} (Heap et al., 2022a). UCS (and therefore Young's modulus) and ITS were measured at ambient laboratory pressure and temperature. These studies concluded that hydrothermal alteration, associated with mineral dissolution, weak secondary minerals (such as clays), and an increase in microstructural heterogeneity, resulted in a reduction in compressive strength (Heap et al., 2021a), tensile strength (Heap et al., 2022a), and Young's modulus (Heap et al., 2021a).

Offcuts from the 19 blocks were crushed and powdered by hand, to a grain size of << 1 mm, using a ceramic pestle and mortar. The whole-rock oxygen isotope ratios of these samples were measured at the University of Cape Town (South Africa) using a Thermo DeltaXP mass spectrometer (data unique to this study). Aliquots of ~10 mg of the whole rock powders were dried overnight at 50 °C and then under vacuum in nickel reaction vessels, then reacted with 30 kPa of ClF_3 for ~4 hours to extract the oxygen from silicates (Borthwick and Harmon, 1982). The extracted oxygen was then converted to CO_2 by passing it over a high-temperature platinised carbon rod. For full analytical details see Vennemann and Smith (1990) and Harris and Vogeli (2010). Unknowns were run with duplicates of the internal quartz standard (MQ), which was used to calibrate the raw data to the SMOW (Standard Mean Ocean Water) scale, using a $\delta^{18}O$ value of 10.1 for MQ (calibrated against NBS-28). The results are reported in standard δ-notation, where $\delta = (R_{sample}/R_{standard} - 1) \times 1000$, R_{sample} is $^{18}O/^{16}O$ in the sample, and $R_{standard}$ is $^{18}O/^{16}O$ relative to SMOW (Gonfiantini, 1978). The analytical reproducibility (assumed here to be similar to the error) is estimated as ± 0.2‰ (2 sigma), based on long-term repeated analysis of MQ.

Hydrogen isotopes and water contents of the same powdered separates were determined using the method of Vennemann and O'Neil (1993). Samples were first melted in quartz glass tubes using a propane torch. The raw data were normalised to SMOW, and corrected for compression, using the water standards RMW (δD = –131.4‰) and CTMP2010 (δD = –7.4‰) with the in-house Serina kaolinite standard analysed with the unknowns (Serina bulk kaolinite, δD = –57‰, H_2O = 12.4 wt%; Harris et al., 1999). The measured δD values of the standard gave an average of –59.5 ± 3.6‰ (2σ, n = 3) after corrections to the raw data. All data were adjusted to the accepted

Serina kaolinite value. Water abundances (as H_2O^+) were measured from the voltage on the mass 2 collector of the mass spectrometer. This was calibrated against measured volumes of standard waters analysed alongside the unknowns. The measured water content of Serina kaolinite gave 12.4 wt% (± 0.5 wt% 2σ, n = 3) (pure kaolinite has an expected water content of 13.95 wt%).

We compare our new data with those for Merapi volcano, collected using the same equipment and techniques described above. For the samples from Merapi volcano, the compressive and tensile strength data were published in Darmawan et al. (2022) and Heap et al. (2022a), respectively, the alteration data (the wt% of secondary minerals, mostly sulfates) were published in Heap et al. (2019, 2022a), and the $\delta^{18}O$ values were published in Darmawan et al. (2022). We have calculated the Young's modulus for the experiments presented in Darmawan et al. (2022) using the pseudo-linear elastic portion of the uniaxial stress-strain curves (these data were not presented in Darmawan et al., 2022).

3 Results

We find that $\delta^{18}O$ values vary from 5.8 to 13.2‰, that δD values vary from –151 to –44‰, and that water contents range from 0.3 to 5.1 wt% for our samples from La Soufrière de Guadeloupe (Table 2). The $\delta^{18}O$ values, δD values, and water content data are plotted in Fig. 2 as a function of secondary alteration mineral content in wt% (Table 2), a metric used in previous studies of these materials (Heap et al., 2021a, 2022a, b). Additionally, we labelled samples with a high content of sulfates (≥ 2 wt% mostly natro-alunite, rarely alunite; Table 1) and opal-A (≥ 10 wt%; Table 1).

Although there is scatter in the data, the $\delta^{18}O$ values positively correlate with the wt% of secondary minerals (Fig. 2a). We note that the two samples rich in opal-A (H20 and H21) plot slightly above the trend delineated by the other data (Fig. 2a). In contrast, no simple correlation is observed for the δD values or the water contents as a function of increasing wt% of secondary minerals (Figs. 2b and 2c, respectively). We highlight that samples with δD values much higher or lower than the other samples are typically samples with a high sulfate content (Figs. 2b). To some extent, this observation also applies to the water content data (Fig. 2c).

Fig. 3 shows the uniaxial compressive strength, tensile strength, and Young's modulus for samples from La Soufrière de Guadeloupe as a function of $\delta^{18}O$ value, δD value, and water content. All these data are provided in an Excel® spreadsheet that accompanies this contribution as Supplementary Information. The data of Fig. 3 show that strength (uniaxial and tensile) and Young's modulus decrease as a function of increasing $\delta^{18}O$ (Figs. 3a,

237 3d, and 3g), but it is more difficult to discern singular trends in the δD and water content data (Figs. 3b, 3c, 3e, 3f,
238 3h, and 3i).
239
240 **4 Discussion**
241 Our data show that the $\delta^{18}O$ values of variably altered rocks from La Soufrière de Guadeloupe increase
242 as a function of increasing alteration (Fig. 2a), as expected for low temperature hydrothermal alteration (≤ 250 °C)
243 (Taylor, 1974; Rose et al., 1994; Donoghue et al., 2010; Darmawan et al., 2022). The dominance of kaolinite, very
244 fine-grained natro-alunite, and amorphous silica, and the absence of smectite (Table 1), suggests alteration at
245 temperatures below 150–200 °C in a steam-heated acid sulfate alteration environment (Zimbelman et al., 2005;
246 Rye, 2005). The least altered samples have stable oxygen isotope compositions (5.8 to 7.3‰) similar to unaltered
247 andesites from La Soufrière de Guadeloupe and other volcanoes in the Eastern Caribbean (Davidson, 1985;
248 Davidson and Harmon, 1989; Van Soest et al., 2002). The highest values of about 12 ± 1‰, in turn, are recorded
249 for the opal-dominated altered rocks. This is consistent with the larger oxygen isotope fractionation between
250 amorphous silica and water (Kita et al., 1985) compared to alunite-water (Stoffregen et al., 1994) and kaolinite-
251 water (Sheppard and Gilg, 1996). The observed positive correlation between $\delta^{18}O$ values and percentage of
252 alteration minerals in our analysed suite can thus be interpreted as a mixing line between primary igneous isotope
253 signatures and secondary alteration phases. The scatter in the data can be explained by (1) the diversity of alteration
254 phases with their distinct oxygen isotope fractionation factors with water, (2) potential temperature variations, (3)
255 variable isotope compositions of the involved fluids, and (4) the location and the type of processes involved in the
256 alteration (e.g., alteration within the host-rock or deep-seated regions of the dome by low temperature steam
257 circulation of hydrothermal fluids in the roots of surficial fumaroles versus surficial alteration within a steaming
258 and cooling dome following emplacement).
259 In contrast to the $\delta^{18}O$ values, no simple correlation is observable for the δD values or water contents as
260 a function of increasing wt% of secondary minerals (Figs. 2b and 2c, respectively). This result is surprising due to
261 the very minor amount of primary hydrogen in these rocks, and the fact that the dominant hydrous alteration phases
262 (alunite group minerals, kaolinite) have similar nominal water contents. Based on the spurious data for samples
263 containing sulfates and/or opal-A (Figs. 2b and 2c), we suspect that the pre-treatment procedure (heating to 200
264 °C in vacuum) probably led to significant water loss in the amorphous silica phase (Brandriss et al., 1998; Martin
265 and Gailliou, 2018) and that future studies should seek alternative methods to measure similar samples. Indeed, if
266 we consider only the samples that contain minor or no sulfates and opal-A (the black symbols in Fig. 2), we observe

positive correlations between the δD values and water contents as a function of increasing wt% of secondary minerals (Figs. 2b and 2c, respectively). This may suggest that our applied extraction technique for hydrogen isotope analysis of (Na-)alunite-rich samples has released sulphur-bearing volatiles that reacted with the dehydroxylation water leading to unreliable water contents and, most probably, hydrogen isotope data (see Rye et al., 1992). Further, for stable hydrogen isotopes, no simple correlation with the percentage of secondary alteration should be expected, as no igneous hydrous minerals were observed even in the least altered samples and the hydrogen isotope composition of the altered rocks will depend on the mineral type, temperature, and water isotope composition rather than simply on the wt% of secondary phases. We further note that the hydrogen isotope compositions of the steam-heated acid chloride-sulfate waters will be influenced by recurrent evaporation and condensation processes and thus may be quite variable (Berg et al., 2018), including positive $d^{18}O$-dD pairs, as also observed for other volcanoes in the Eastern Caribbean (Chiodini et al., 1996; Joseph et al., 2011). Furthermore, the D/H fractionation factors between some of the dominant hydrous phases and water are either less well constrained (e.g., alunite; Stoffregen et al. 1994) or even unknown (e.g., amorphous silica).

Although there are some outliers, Figs. 3a, 3d, and 3g show that the uniaxial compressive strength, tensile strength, and Young's modulus of variably altered rocks from La Soufrière de Guadeloupe and Merapi volcano decrease as a function of increasing $\delta^{18}O$ value. Therefore, strength and Young's modulus are decreasing as a function of increasing alteration, as discussed in Heap et al. (2021a) and Darmawan et al. (2022). However, we find little to no correlation between strength and Young's modulus and the δD value (Figs. 3b, 3e, and 3h) or water content (Figs. 3c, 3f, and 3i), likely due to the pre-treatment of the samples at 200 °C. As noted above, the δD values are not related to the wt% of secondary alteration phases, and thus alteration intensity, and the measured water contents depend on the alteration mineral type. Therefore, we will focus here on using $\delta^{18}O$ as a proxy for strength and Young's modulus. Although we focus here on $\delta^{18}O$ only, we do not rule out the possibility of using δD and/or water contents to predict rock properties in the future, as long as alternate laboratory methods are used (those that avoid pre-treating the samples at 200 °C, but can remove extraneous absorbed water).

Figs. 4a, 4b, and 4c show uniaxial compressive strength, tensile strength, and Young's modulus, respectively, as a function of $\delta^{18}O$. The outliers in these data, shown as grey circles in Fig. 4, include samples from blocks H14, H29, and H32. Blocks H14 and H29 contained mesoscale fractures, which could explain their low strength and Young's modulus (Heap et al., 2021a, 2022a). Block H32, which is much stronger than the other blocks (Fig. 4), was collected from an older (K-Ar age 0.079 ± 0.003 Ma; Carlut and Quidelleur, 2000), low-porosity, and very thick lava adjacent to the Galion waterfall (Fig. 1). Therefore, the alteration history of this block

differs from the other blocks collected on, within, or adjacent to, the present-day dome that was emplaced during the 1530 CE eruption nearly 500 years ago (Fig. 1). Excluding these outliers, we provide best-fit linear functions to the entire dataset (La Soufrière de Guadeloupe and Merapi volcano) in Fig. 4. Uniaxial compressive strength, σ_c, indirect tensile strength, σ_t, and Young's modulus, E, can therefore be estimated using the following empirical equations (where strength is in MPa, Young's modulus in GPa, and $\delta^{18}O$ in ‰):

$$\sigma_c = -13.8(\delta^{18}O) + 204.7 \quad (1)$$

$$\sigma_t = -0.70(\delta^{18}O) + 13.1 \quad (2)$$

$$E = -3.42(\delta^{18}O) + 54.0 \quad (3)$$

Estimates of the strength (compressive and tensile) and Young's modulus of volcanic rocks are required in a range of laboratory- and large-scale modelling designed to understand, respectively, the mechanical behaviour of volcanic rocks and the stability of volcanic flanks and domes (Watters et al., 2000; Okubu, 2004; Apuani et al., 2005; Moon et al., 2005; del Potro and Hürlimann, 2008; Heap et al., 2021a, b; Heap and Harnett, 2021; Wallace et al., 2021). We show here that rock physical and mechanical property estimates for volcano stability modelling, important assess volcanic hazards and mitigate risk, can be provided using Eqs. (1), (2), and (3) by measuring the $\delta^{18}O$ values of representative samples collected from the flank or dome of a volcano. Composite $\delta^{18}O$-value cross-sections of volcanoes (Rose et al., 1994) and $\delta^{18}O$ values determined from borehole drill cuttings (Hattori and Muehlenbachs, 1982) could also be used to prepare strength and Young's modulus maps and profiles, respectively. Unlike laboratory experiments, which require reasonably large blocks from which to prepare the experimental samples, the approach to estimate strength and Young's modulus outlined herein, i.e. Eqs. (1), (2), and (3), requires only < 1 g of material (as representative as possible; e.g., using a < 1 g aliquot of a larger mass of well-mixed powdered material, if available) and is thus ideally suited to provide rock physical and mechanical property estimates when only limited material is available, such as drill cuttings form boreholes or when sampling large blocks is impracticable.

The three-dimensional structures and rock property distributions inside volcanic systems are usually inferred using targeted geophysical methods. Electrical methods, such as magnetotellurics and electrical resistivity tomography, have shown to be particularly useful to infer rock alteration distributions in hydrothermal systems because of the influence of secondary minerals in the bulk electrical conductivity of rocks (Rosas-Carbajal et al., 2016; Byrdina et al., 2018; Finn et al., 2022). Petrophysical relations that link these properties are, however, far

from obvious. The difficulty in establishing simple relations between electrical conductivity and the percentage of alteration minerals seems to arise also from the dependence on the type of alteration (i.e. mineral composition), temperature, and fluid composition (Lévy et al., 2018; Ghorbani et al., 2018), similar to what we suggest may happen for whole-rock oxygen isotope. Thus, it may be interesting to compare the whole-rock oxygen isotope and the electrical conductivity dependence for different degrees of altered volcanic rocks. Having both properties measured for representative volcano samples could significantly improve the upscaling of the physical properties measured in the laboratory to the field-scale three-dimensional models obtained by geophysical methods.

Although we focus here on volcanological applications, our approach could be used to provide rock physical and mechanical property estimates for borehole stability assessments and stimulation strategies in volcanic geothermal reservoirs, which typically comprise altered rocks (Siratovich et al., 2014; Cant et al., 2018; Lévy et al., 2018). Whole-rock $\delta^{18}O$ values are also often used in mineral exploration (Green et al., 1983; Criss et al., 1985; Cathles, 1993; Paradis et al., 1993; Lentz, 1999), and could therefore also be used to provide rock physical and mechanical property estimates for rock drillability estimates and underground excavation stability assessments during mineral exploration and extraction in volcanic terrains.

One drawback of our approach, however, is that our analysis (Fig. 4) has been performed on rocks that show a decrease in strength and Young's modulus as a result of hydrothermal alteration (Heap et al., 2021a, 2022a; Darmawan et al., 2022). However, hydrothermal alteration associated with pore- and crack-filling precipitation can increase strength and Young's modulus (Marmoni et al., 2017; Heap et al., 2020b, 2021b). As a result, care should be taken when using Eqs. (1), (2), and (3) to ensure that the alteration observed in a particular setting does not appear to strengthen or harden the rock. Care should also be taken to ensure that the alteration is indeed low temperature ($\leq$ 250 °C) hydrothermal alteration, and that the rocks have not undergone alteration at higher temperatures, which will decrease whole-rock $\delta^{18}O$ values. Therefore, a detailed study of the mineral assemblage is required in order to use Eqs. (1), (2), and (3) confidently. To improve our approach to estimate rock physical and mechanical properties using $\delta^{18}O$ values, more data are required for a wider variety of hydrothermally altered rocks, including those with different alteration mineral assemblages (e.g., those containing smectite). We further note that the analysis presented here provides laboratory-scale values of strength and Young's modulus, and so these values likely require upscaling before they are used in large-scale volcano models. Strength can be upscaled using, for example, the Hoek-Brown failure criterion (Hoek et al., 2002) and Young's modulus can be upscaled using the Hoek-Diederichs equation (Hoek and Diederichs, 2006; Heap et al., 2020a).

5 Concluding remarks

Rock physical and mechanical properties are required for large-scale models designed to assess the stability of a lava dome or volcanic flank (Watters et al., 2000; Okubu, 2004; Apuani et al., 2005; Moon et al., 2005; del Potro and Hürlimann, 2008; Heap et al., 2021a, b; Heap and Harnett, 2021; Wallace et al., 2021). The ubiquity of hydrothermal alteration at active volcanoes (Aizawa et al., 2009; Rosas-Carbajal et al., 2016; Byrdina et al., 2017, 2018; Finn et al., 2018; Tseng et al., 2020; Kereszturi et al., 2021; Finn et al., 2022), and evidence suggesting that alteration compromises volcano stability (van Wyk de Vries et al., 2000; Voight et al., 2002; Salaün et al., 2011), underscores the need for not only understanding the influence of alteration on rock physical and mechanical properties, but also for well constrained properties for altered volcanic rocks, data that are currently rare. In certain scenarios, such as when rock blocks large enough for laboratory experiments cannot be acquired (e.g., drill cuttings from boreholes, when the material is too friable or delicate to prepare samples for laboratory experiments, or when it is impracticable to sample and export a sufficient number of large blocks), or when laboratory equipment is not available, an independent measure of alteration that can be used to estimate the required rock physical and mechanical properties would be extremely useful for routine volcano stability modelling. Such a method could also be used to estimate pre-failure rock properties from semi-consolidated friable material found in debris avalanches. Here we show that whole-rock $\delta^{18}O$ values, a method that requires a very small amount of representative material, can be used to estimate the strength (compressive and tensile) and Young's modulus of low-temperature ($\leq$ 150-200 °C) hydrothermally (acid-chloride-sulfate) altered dome rocks. Based on the promise of the approach documented herein, we recommend that future studies further explore the relationship between whole-rock $\delta^{18}O$ values and the physical and mechanical properties of altered rocks with different alteration assemblies (such as those that contain smectites).

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Statements and Declarations

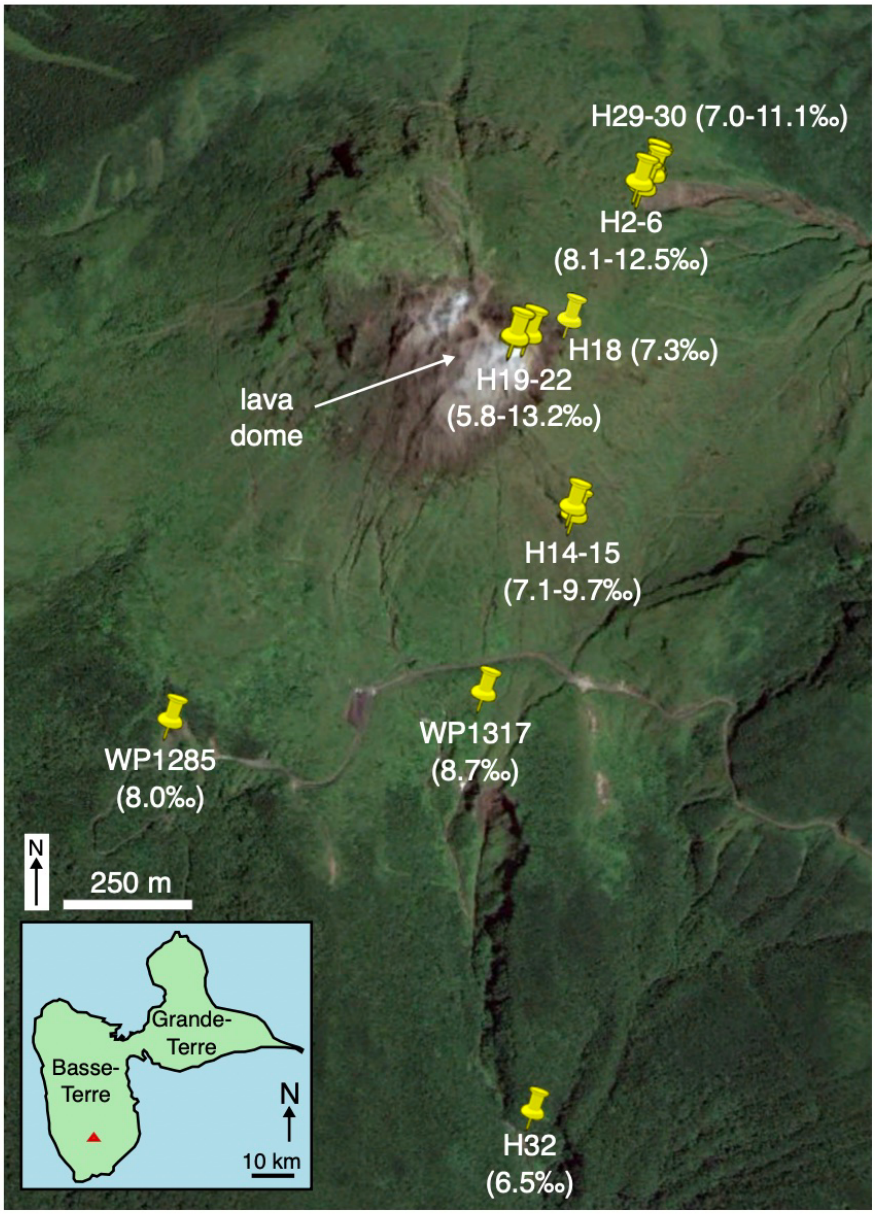
The authors declare no financial or non-financial interests that are directly or indirectly related to this work.

Supplementary Information

We provide an Excel® spreadsheet that contains the data collected for, and analysed in, this contribution.

Author contributions

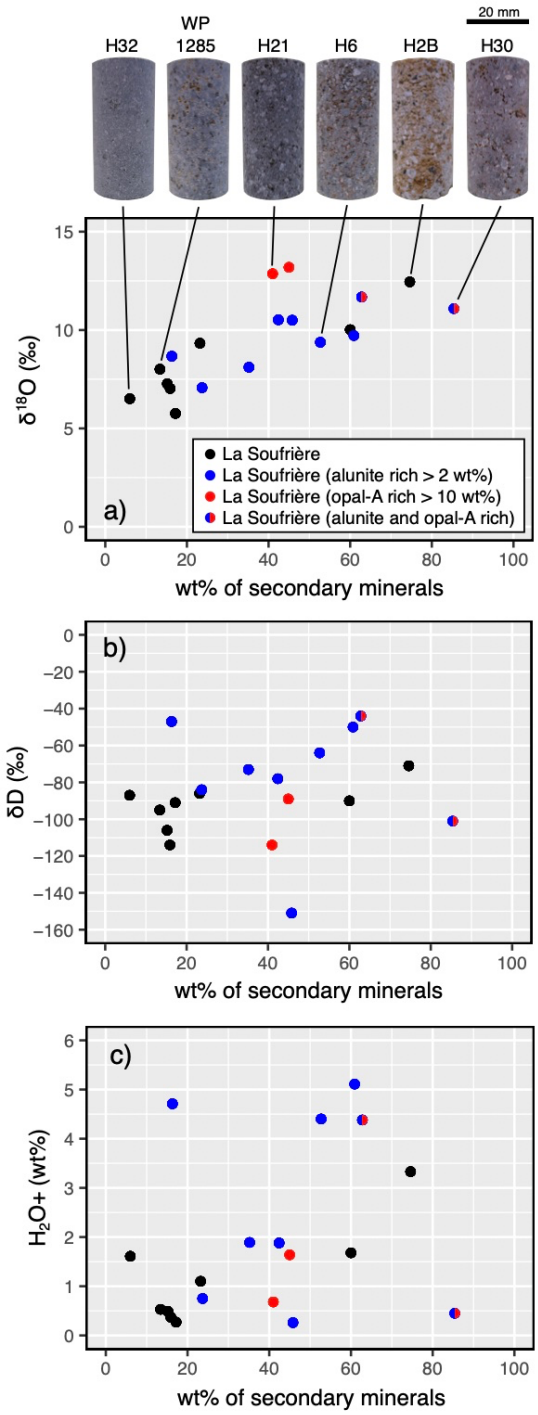
Michael Heap and Valentin Troll conceived the idea for this study. Rock samples were collected by Michael Heap, Marina Rosas-Carbajal, Jean-Christophe Komorowski, and Patrick Baud. Mechanical laboratory experiments were performed by Michael Heap. Isotope analyses were performed by Chris Harris. Isotope data were discussed and analysed by Chris Harris, Albert Gilg, Roberto Moretti, and Valentin Troll. Michael Heap wrote the manuscript, with contributions from all authors. All authors read and approved the final manuscript.



406

407 **Fig. 1.** Google Earth image (Google Maxar Technologies CNES / Airbus) of La Soufrière de Guadeloupe (Eastern
408 Caribbean) showing the sampling locations for the 19 rock blocks collected for this study (see text for details).
409 Whole-rock $\delta^{18}O$ values, measured in this study (Table 2) are given next to sampling location. Inset shows a map
410 of Guadeloupe in which the location of La Soufrière de Guadeloupe is indicated by a red triangle.

411



412

413 **Fig. 2**. Whole-rock $\delta^{18}O$ value (a), whole-rock δD value (b), and water content (c) as a function of the wt% of
414 secondary minerals for rocks from La Soufrière de Guadeloupe (Eastern Caribbean; sulfate-rich samples (≥ 2 wt%)
415 are blue, opal-rich samples (≥ 10 wt%) are red, samples that are both sulfate- and opal-rich are blue and red, and
416 all other samples are black) (alteration data from Heap et al., 2021a, 2022a, b). Photographs of 20 mm-diameter
417 cylindrical samples cored from selected blocks (those that preserve different degrees of alteration) are provided in
418 panel (a). Experimental errors are within the size of the symbols. All these data are provided in an Excel®
419 spreadsheet that accompanies this contribution as Supplementary Information.

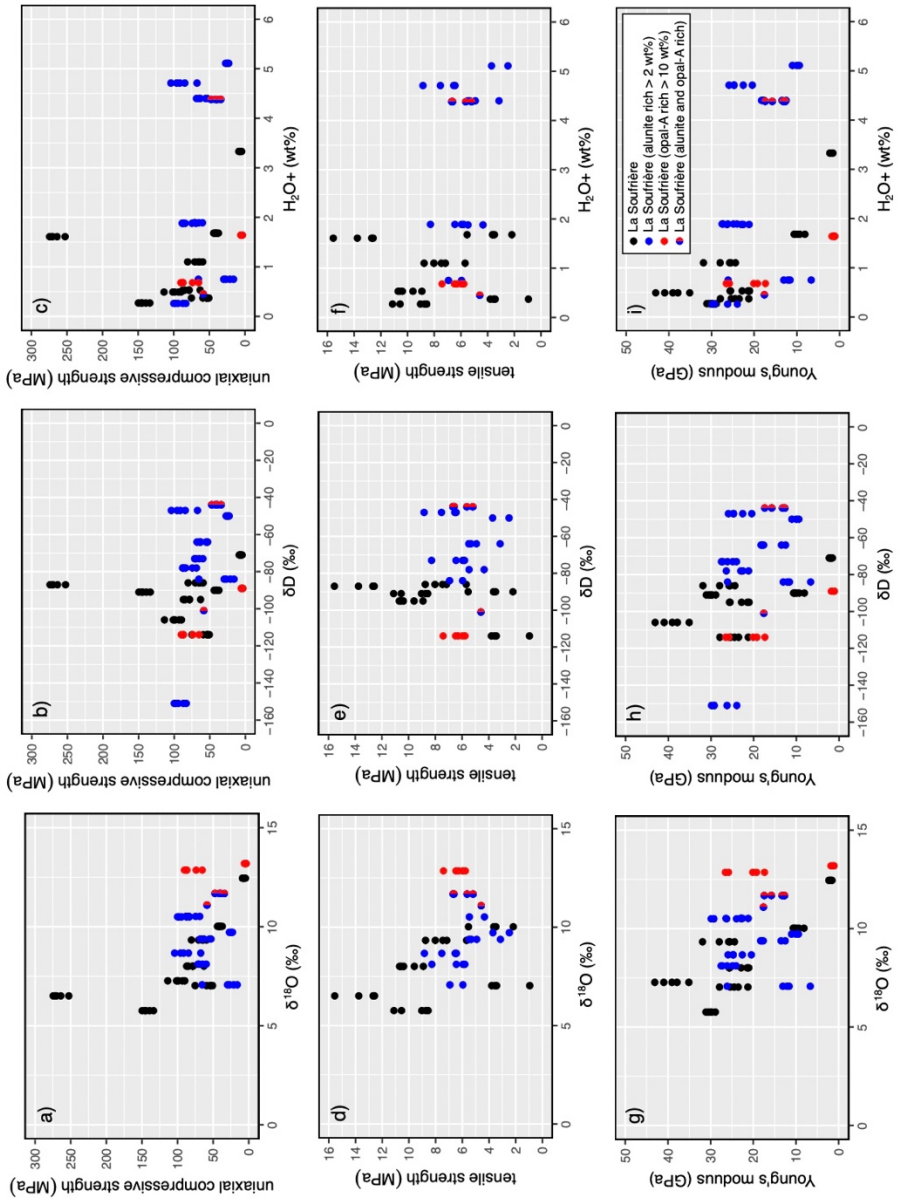


Fig. 3. Uniaxial compressive strength as a function of $\delta^{18}O$ value (a), δD value (b), and water content (c) for rocks from La Soufrière de Guadeloupe (Eastern Caribbean; sulfate-rich samples (≥ 2 wt%) are blue, opal-rich samples (≥ 10 wt%) are red, samples that are both sulfate- and opal-rich are blue and red, and all other samples are black). Indirect tensile strength as a function of $\delta^{18}O$ value (d), δD value (e), and water content (f). Young's modulus as a function of $\delta^{18}O$ value (g), δD value (h), and water content (i). The strength (compressive and tensile) and Young's modulus data are taken from Heap et al. (2021a, 2022a). Uniaxial compressive strength, tensile strength, and Young's modulus were measured on multiple core samples prepared from each block, which is characterised by a single $\delta^{18}O$ value, δD value, and water content. Experimental errors are within the size of the symbols. All these data are provided in an Excel® spreadsheet that accompanies this contribution as Supplementary Information.

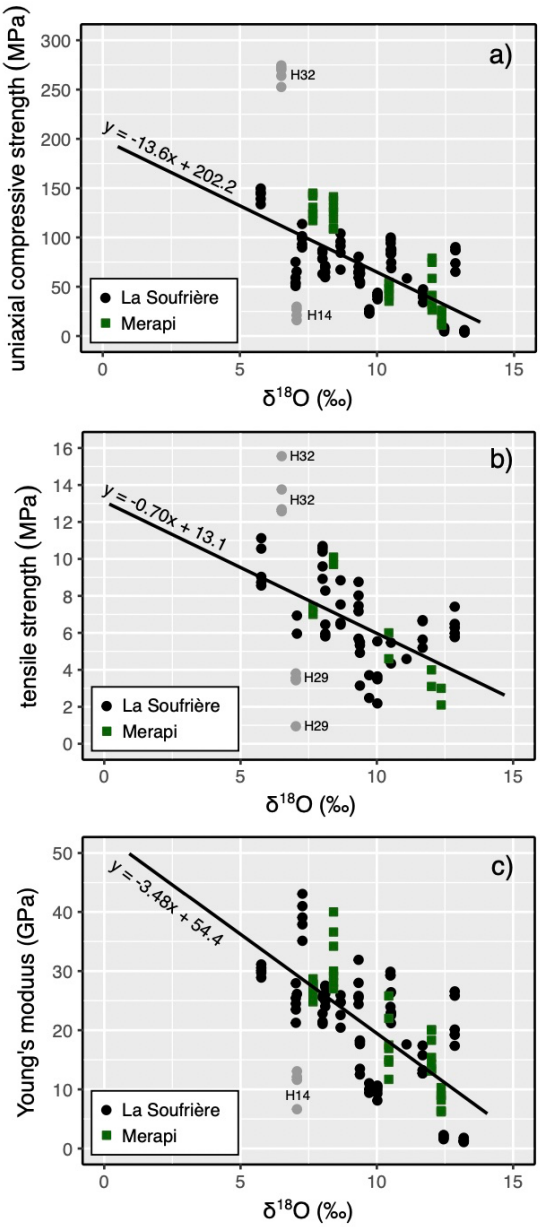


Fig. 4. Uniaxial compressive strength (a), indirect tensile strength (b), and Young's modulus (c) as a function of whole-rock $\delta^{18}O$ values for rocks from La Soufrière de Guadeloupe (Eastern Caribbean; black circles; strength and Young's modulus data from Heap et al., 2021a, 2022a) and Merapi volcano (Indonesia; green squares; data from Heap et al., 2019, 2022a; Darmawan et al., 2022). Data outliers are shown in grey (see text for details). Black lines – best-fit linear functions, Eqs. (1), (2), and (3) for the La Soufrière de Guadeloupe and Merapi volcano data (excluding the outliers shown in grey). The coefficient of determination for the data of panels (a), (b), and (c) are 0.52, 0.36, and 0.52, respectively. Uniaxial compressive strength, tensile strength, and Young's modulus were measured on multiple core samples prepared from each block, which is characterised by a single $\delta^{18}O$ value. Experimental errors are within the size of the symbols. All these data are provided in an Excel® spreadsheet that accompanies this contribution as Supplementary Information.

Mineral	H2A	H2B	H3	H4A	H5A	H6	H14	H15	H18	H19	H20	H21	H22	H25	H29	H30	H32	WP1285	WP1317
Plagioclase	56.7	12.3	46.6	23.3	41.3	30.0	60.7	22.5	61.2	22.0	28.7	24.2	59.5	38.7	62.4	8.9	64.4	64.7	61.6
Clinopyroxene	8.7	3.4	5.6	4.9	5.2	6.4	6.3	7.3	8.4	5.0	8.9	12.4	8.9	5.3	7.8	2.5	9.5	5.2	5.9
Orthopyroxene	10.8	9.5	11.8	11.8	11.1	10.8	8.6	9.2	12.2	10.2	15.0	19.3	13.6	10.2	11.2	3.3	15.1	13.2	15.6
(Ti-) Magnetite	0.7	-	0.8	-	-	-	0.8	-	2.9	-	2.4	3.1	0.8	-	2.7		4.9	3.5	0.7
Quartz*	1.0	0.5	0.6	0.6	0.5	0.5	1.7	0.7	0.7	1.7	0.3	0.2	0.6	0.3	0.4	0.9	0.3	0.2	0.7
Cristobalite*	11.3	12.8	10.6	11.8	13.0	11.1	13.5	10.2	11.7	9.5	11.4	11.7	10.6	9.8	12.4	9	5.7	-	-
Tridymite*	-	-	-	-	-	-	-	0.7	-	-	-	-	-	-	-			13.2	13.2
Hematite*	-	-	-	-	-	-	3.4	-	2.8	2.4	-	-	-	-	3.1	4.3		-	-
Pyrite*	3.5	-	3.8	2.3	-	-	-	-	-	-	-	0.4	3.1	0.6	-			-	-
Alunite*	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			-	2.4
Na-Alunite*	1.4	1.6	2.8	1.3	5.4	5.1	5.1	15.0	-	14.2	0.5	0.5	-	9.8	-	25.6		-	-
Gypsum*	-	-	-	0.7	-	-	-	-	-	-	0.8	1.2	-	-	-			-	-
Kaolinite*	6	59.7	17.4	43.3	23.5	36.0	< 1	34.3	-	2.0	2.0	2.0	< 1	25.3	-	35.6		-	-
Talc*	-	-	-	-	-	-	-	-	-	-	-	-	2.9	-	-			-	-
Opal-A*	-	-	-	-	-	-	-	-	-	33	30	25	-	-	-	10		-	-

Table 1. Mineral contents of the 19 rock blocks from La Soufrière de Guadeloupe measured by X-ray powder diffraction. Values in wt%. Asterisk denotes a secondary mineral (i.e. alteration mineral). Data for H30 and H32 were published in Heap et al. (2022b). All other data were published in Heap et al. (2021a). The relative errors in the quantification are in the order of 5–10%.

Volcano	Block	Weight percentage of secondary minerals	$\delta^{18}O$ (‰)	δD (‰)	H_2O+ (wt%)
La Soufrière	H2A	23	9.3	–86	1.1
La Soufrière	H2B	75	12.5	–71	3.3
La Soufrière	H3	35	8.1	–73	1.9
La Soufrière	H4A	60	10.0	–90	1.7
La Soufrière	H5A	42	10.5	–78	1.9
La Soufrière	H6	53	9.4	–64	4.4
La Soufrière	H14	24	7.1	–84	0.8
La Soufrière	H15	61	9.7	–50	5.1
La Soufrière	H18	15	7.3	–106	0.5
La Soufrière	H19	63	11.7	–44	4.4
La Soufrière	H20	45	13.2	–89	1.6
La Soufrière	H21	41	12.9	–114	0.7
La Soufrière	H22	17	5.8	–91	0.3
La Soufrière	H25	46	10.5	–151	0.3
La Soufrière	H29	16	7.0	–114	0.4
La Soufrière	H30	85	11.1	–101	0.5
La Soufrière	H32	6	6.5	–87	1.6
La Soufrière	WP1285	13	8.0	–95	0.5
La Soufrière	WP1317	16	8.7	–47	4.7
Merapi	MU	8	7.7	NA	NA
Merapi	MSA1	33	12.4	NA	NA
Merapi	MSA2	29	8.4	NA	NA
Merapi	MHA1	45	10.4	NA	NA
Merapi	MHA2	62	12.0	NA	NA

Table 2. The weight percentage of secondary minerals (data from Heap et al., 2021a, 2022a, b), whole-rock $\delta^{18}O$ values, whole-rock δD values, and water content (H_2O+) for rocks from La Soufrière de Guadeloupe (Eastern Caribbean) and Merapi volcano (Indonesia; data from Darmawan et al., 2022; Heap et al., 2019, 2022a). The sampling locations for the blocks from La Soufrière de Guadeloupe are shown in Fig. 1. NA – not analysed

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