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## CO<sub>2</sub> flux emissions from the Earth's most actively degassing volcanoes, 2005–2015

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The global carbon dioxide (CO<sub>2</sub>) flux from subaerial volcanoes remains poorly quantified, limiting our understanding of the deep carbon cycle during geologic time and in modern Earth. Past attempts to extrapolate the global volcanic CO<sub>2</sub> flux have been biased by observations being available for a relatively small number of accessible volcanoes. Here, we propose that the strong, but yet unmeasured, CO<sub>2</sub> emissions from several remote degassing volcanoes worldwide can be predicted using regional/global relationships between the CO<sub>2</sub>/S<sub>T</sub> ratio of volcanic gases and whole-rock trace element compositions (e.g., Ba/La). From these globally linked gas/rock compositions, we predict the CO<sub>2</sub>/S<sub>T</sub> gas ratio of 34 top-degassing remote volcanoes with no available gas measurements. By scaling to volcanic SO<sub>2</sub> fluxes from a global catalogue, we estimate a cumulative “unmeasured” CO<sub>2</sub> output of  $11.4 \pm 1.1$  Mt/yr (or  $0.26 \pm 0.02 \cdot 10^{12}$  mol/yr). In combination with the measured CO<sub>2</sub> output of  $27.4 \pm 3.6$  Mt/yr (or  $0.62 \pm 0.08 \cdot 10^{12}$  mol/yr), our results constrain the time-averaged (2005–2015) cumulative CO<sub>2</sub> flux from the Earth's 91 most actively degassing subaerial volcanoes at  $38.7 \pm 2.9$  Mt/yr (or  $0.88 \pm 0.06 \cdot 10^{12}$  mol/yr).

Volcanism is the primary mechanism through which carbon (C) stored in the deep Earth<sup>1,2</sup> is transferred to surface environments to feed C exchanges in the atmosphere-ocean-biosphere system<sup>3</sup>. Over geological time, volcanic CO<sub>2</sub> emissions have been a key control on atmospheric-oceanic CO<sub>2</sub> levels<sup>4–8</sup>, ultimately regulating evolution of climate and life on our planet<sup>9,10</sup>.

The global volcanic CO<sub>2</sub> flux in modern Earth remains inadequately known<sup>11,12</sup> and, ironically, is less constrained for subaerial volcanoes than for the less-accessible mid-ocean ridges, for which the <sup>3</sup>He flux<sup>13</sup> or the CO<sub>2</sub>/Ba ratio<sup>14</sup> proxies have successfully been applied. Direct volcanic CO<sub>2</sub> observations at subaerial volcanoes are technically challenging from both ground<sup>11,15</sup> and space<sup>16</sup> due to the large atmospheric CO<sub>2</sub> burden, and thus remain limited in number<sup>17,18</sup>. The volcanic CO<sub>2</sub> flux can be quantified indirectly by combining simultaneous acquisitions of UV-sensed sulphur dioxide (SO<sub>2</sub>) fluxes<sup>11,15,19,20</sup> and gas compositions (CO<sub>2</sub>/SO<sub>2</sub> ratios), but gas observational networks are still in a developing stage<sup>21,22</sup>, resulting in sparse and incomplete gas catalogues<sup>23,24</sup>. CO<sub>2</sub> flux data have so far been obtained<sup>11,15</sup> for only <60 of the several hundred currently degassing Holocene volcanoes<sup>25</sup>. CO<sub>2</sub> flux records are continuous enough only for a few (<10) volcanoes where permanent instrumentation is operating<sup>26–29</sup>, while sparse results (one or a few campaign-style measurements at most) are available for the remaining ~50. In addition, scarce or even no information exists for several top-ranking degassing volcanoes<sup>30</sup> in remote regions of the world (e.g., Vanuatu<sup>31</sup>, Papua New Guinea, the Solomon arc, and the Sunda-Banda arc in Indonesia<sup>32,33</sup>). Attempts to extrapolate available measurements to all the subaerial degassing volcanoes have been problematic<sup>11,23</sup> and require use of questionable statistical approaches<sup>34,35</sup>. Estimates of the global volcanic CO<sub>2</sub> flux thus vary widely, from 66 to 540 Mt/yr<sup>11,23</sup>.

Ideally, refining the volcanic CO<sub>2</sub> inventory would require a comprehensive record comprising simultaneous composition/emission measurements for all the currently active strong volcanic gas emitters globally. The top-degassing volcanic targets during 2005–2015 (Table 1) have recently been identified<sup>30</sup> from satellite-based observations of the SO<sub>2</sub> flux using the Ozone Mapping Instrument (OMI). Carn *et al.* (ref.<sup>30</sup>) identified 91 volcanoes, listed in Table 1, releasing SO<sub>2</sub> at rates above the OMI detection limit of 16 tons/day. Gas CO<sub>2</sub>/S<sub>T</sub> ratios (where S<sub>T</sub> is Total Sulfur, corresponding to SO<sub>2</sub> in these strongly degassing magmatic-volatile emitting volcanoes) are available for 57 out of these 91 volcanic sources<sup>36</sup>, from which SO<sub>2</sub> fluxes can straightforwardly be converted

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|       | Measured volcanoes                     |             |        |         |  |      |   |  |     |  |                                |      |   |
|-------|--|-------------|--------|---------|--|------|---|--|-----|--|--------------------------------|------|---|
| A     | B                                      | B           | D      | E       | F  | G    | H   | K  | I   | L = F × H                                | M = F × K                      | N    | O   |
| Group | Volcano                                | Country     | Lat    | Long    | Measured SO <sub>2</sub> flux (tons/day) | SD   | Measured CO <sub>2</sub> /SO <sub>2</sub> (molar) | Predicted CO <sub>2</sub> /SO <sub>2</sub> (molar) | SD  | Measured CO <sub>2</sub> flux (tons/day) | Predicted CO <sub>2</sub> flux | SD   | Notes/Data Sources  |
| 1     | Ambrym                                 | Vanuatu     | −16.25 | 168.12  | 7356                                     | 3168 | 1.5   | —  | 0.4 | 7586                                     | —                              | 3843 |   |
| 1     | Asama                                  | Japan       | 36.40  | 138.53  | 449                                      | 430  | 0.8   | —  | 0.2 | 247                                      | —                              | 247  |   |
| 1     | Aso                                    | Japan       | 32.88  | 131.11  | 628                                      | 492  | 1.8   | —  | 0.5 | 777                                      | —                              | 650  |   |
| 1     | Augustine                              | USA         | 59.35  | −153.45 | 73                                       | 140  | 1.5   | —  | 0.7 | 75                                       | —                              | 148  |   |
| 1     | Avachinsky                             | Russia      | 53.25  | 158.83  | 707                                      | 619  | 1.2*  | —  | 0.3 | 584                                      | —                              | 531  | *Ref. <sup>110</sup>  |
| 1     | Chikurachki + Ebeko <sup>5</sup>       | Russia      | 50.33  | 155.46  | 496                                      | 469  | 0.9*  | —  | 0.3 | 320                                      | —                              | 317  | *Ref. <sup>111</sup>  |
| 1     | Cleveland                              | USA- AK     | 52.83  | −169.77 | 152                                      | 142  | 1.0*  | —  | 0.3 | 105                                      | —                              | 102  | *Upper limit from ref. <sup>111</sup>   |
| 1     | Copahue                                | Argentina   | −37.86 | −71.16  | 341                                      | 425  | 0.9   | —  | 0.3 | 211                                      | —                              | 272  |   |
| 1     | Dukono                                 | Indonesia   | 1.68   | 127.88  | 1726                                     | 611  | 0.4   | —  | 0.1 | 475                                      | —                              | 206  |   |
| 1     | Gareloi                                | USA- AK     | 51.79  | −178.79 | 52                                       | 47   | 0.5   | —  | 0.1 | 18                                       | —                              | 17   |   |
| 1     | Isluga                                 | Chile       | −19.15 | −68.83  | 78                                       | 107  | 1.0   | —  | 0.0 | 51                                       | —                              | 70   |   |
| 1     | Kliuchevskoi + Bezymianny <sup>5</sup> | Russia      | 56.06  | 160.64  | 580                                      | 461  | 1.3*  | —  | 0.4 | 519                                      | —                              | 442  | *Assumes equal flux for the 2 volcanoes   |
| 1     | Krakatau                               | Indonesia   | −6.11  | 105.42  | 303                                      | 252  | 0.4   | —  | 0.1 | 83                                       | —                              | 73   |   |
| 1     | Kudriavyy                              | Russia      | 45.39  | 148.84  | 187                                      | 103  | 0.9   | —  | 0.3 | 116                                      | —                              | 72   |   |
| 1     | Lastarria                              | Argentina   | −25.17 | −68.50  | 248                                      | 62   | 1.6   | —  | 0.4 | 273                                      | —                              | 96   |   |
| 1     | Miyake-jima                            | Japan       | 34.08  | 139.53  | 1018                                     | 934  | 0.7   | —  | 0.2 | 490                                      | —                              | 471  |   |
| 1     | Mutnovsky + Gorely <sup>5</sup>        | Russia      | 52.45  | 158.20  | 753                                      | 690  | 1.7*  | —  | 0.5 | 880                                      | —                              | 847  | *Assumes equal flux for the 2 volcanoes   |
| 1     | Pagan                                  | Marianas    | 18.14  | 145.79  | 583                                      | 547  | 0.8   | —  | 0.2 | 321                                      | —                              | 311  |   |
| 1     | Redoubt                                | USA         | 60.49  | −152.75 | 368                                      | 1051 | 1.0   | —  | 0.2 | 253                                      | —                              | 724  |   |
| 1     | Sabancaya                              | Peru        | −15.80 | −71.86  | 87                                       | 158  | 1.5   | —  | 0.1 | 90                                       | —                              | 163  |   |
| 1     | Sakura-jima                            | Japan       | 31.59  | 130.66  | 1056                                     | 757  | 0.9   | —  | 0.3 | 653                                      | —                              | 516  |   |
| 1     | San Miguel                             | El Salvador | 13.42  | −88.47  | 88                                       | 134  | 1.5   | —  | 0.2 | 91                                       | —                              | 139  |   |
| 1     | Santa Ana                              | El Salvador | 13.85  | −89.63  | 97                                       | 180  | 1.0   | —  | 0.3 | 66                                       | —                              | 125  |   |
| 1     | Satsuma-lojima                         | Japan       | 30.79  | 130.31  | 585                                      | 190  | 0.4   | —  | 0.1 | 161                                      | —                              | 70   |   |
| 1     | Shishaldin                             | USA- AK     | 54.76  | −163.97 | 347                                      | 278  | 1.4*  | —  | 0.4 | 334                                      | —                              | 284  | *ref. <sup>112</sup>  |
| 1     | Shiveluch                              | Russia      | 56.64  | 161.34  | 530                                      | 284  | 1.3*  | —  | 0.4 | 473                                      | —                              | 289  | *gas data for Klyucheskoy are used  |
| 1     | Spurr                                  | USA         | 61.30  | −152.25 | 106                                      | 106  | 1.1   | —  | 0.3 | 80                                       | —                              | 83   |   |
| 1     | Suwanose-jima                          | Japan       | 29.64  | 129.72  | 863                                      | 314  | 1.0   | —  | 0.3 | 593                                      | —                              | 280  |   |
| 1     | Tokachi                                | Japan       | 43.42  | 142.69  | 135                                      | 98   | 0.4   | —  | 0.1 | 37                                       | —                              | 29   |   |
| 1     | Turrialba + Poas                       | Costa Rica  | 10.03  | −83.77  | 751                                      | 681  | 1.0 (3.4*)  | —  | 0.8 | 1756                                     | —                              | 1644 | *Mean (2002–2017) Turrialba composition from de Moor <i>et al.</i> , Pers. Comm.. |
| 1     | Villarrica                             | Chile       | −39.42 | −71.93  | 281                                      | 160  | 1.0   | —  | 0.3 | 193                                      | —                              | 124  |   |
| 1     | Yasur                                  | Vanuatu     | −19.53 | 169.44  | 1408                                     | 563  | 1.6   | —  | 0.4 | 1549                                     | —                              | 730  |   |
| 2     | Galeras                                | Colombia    | 1.20   | −77.39  | 218                                      | 317  | 3.3   | —  | 0.5 | 495                                      | —                              | 723  |   |
| 2     | Lokon-Empung                           | Sulawesi    | 1.36   | 124.79  | 204                                      | 154  | 3.2*  | —  | 1.0 | 449                                      | —                              | 366  | *This study   |
| 2     | Masaya                                 | Nicaragua   | 11.98  | −86.16  | 867                                      | 364  | 2.7   | —  | 0.7 | 1610                                     | —                              | 794  |   |
| 2     | Mayon                                  | Philippines | 13.26  | 123.69  | 453                                      | 274  | 2.4   | —  | 0.7 | 747                                      | —                              | 501  | *ref. <sup>113</sup>  |
| 2     | Nevado del Huila                       | Colombia    | 2.93   | −76.03  | 627                                      | 665  | 2.0   | —  | 0.6 | 862                                      | —                              | 947  |   |
| 2     | Nevado del Ruiz                        | Colombia    | 4.90   | −75.32  | 1074                                     | 1376 | 3.0   | —  | 0.5 | 2215                                     | —                              | 2862 |   |
| 2     | Raung + Ijen                           | East Java   | −8.06  | 114.24  | 631                                      | 238  | 2.6*  | —  | 0.5 | 1111                                     | —                              | 472  | *Uses composition of Ijen only (ref. <sup>114</sup> )                             |
| 2     | San Cristobal + Telica                 | Nicaragua   | 12.70  | −87.00  | 621                                      | 283  | 3.5*  | —  | 2.0 | 1494                                     | —                              | 1092 | *Assumes equal flux for the 2 volcanoes   |
| 2     | Sirung                                 | Pantar      | −8.51  | 124.13  | 373                                      | 162  | 3.2*  | —  | 2.0 | 820                                      | —                              | 624  | *ref. <sup>115</sup>  |
| 2     | Soufriere Hills                        | Montserrat  | 16.72  | −62.18  | 1296                                     | 761  | 3.0   | —  | 1.1 | 2672                                     | —                              | 1851 |   |
| 2     | Ubina                                  | Peru        | −16.34 | −70.90  | 222                                      | 252  | 2.4   | —  | 0.5 | 367                                      | —                              | 423  |   |
| 2     | White Island                           | New Zealand | −37.52 | 177.18  | 254                                      | 107  | 4.0   | —  | 1.2 | 699                                      | —                              | 362  |   |
| 3     | Bromo + Semeru                         | Java        | −7.94  | 112.95  | 775                                      | 298  | 4.1*  | —  | 0.7 | 2184                                     | —                              | 920  | *Uses Bromo gas composition   |
| 3     | Etna                                   | Italy       | 37.73  | 15.00   | 2032                                     | 517  | 6.5   | —  | 2.2 | 9083                                     | —                              | 3844 |   |
| 3     | Merapi                                 | Java        | −7.56  | 110.44  | 32                                       | 51   | 4.7   | —  | 0.5 | 104                                      | —                              | 165  |   |

Continued

| Measured volcanoes   |                             |                          |        |         |  |      |   |  |     |  |   |       |   |
|--|-----------------------------|--------------------------|--------|---------|--|------|---|--|-----|--|---|-------|---|
| A  | B                           | B                        | D      | E       | F  | G    | H   | K  | I   | L = F × H                                | M = F × K                                 | N     | O   |
| Group  | Volcano                     | Country                  | Lat    | Long    | Measured SO <sub>2</sub> flux (tons/day) | SD   | Measured CO <sub>2</sub> /SO <sub>2</sub> (molar) | Predicted CO <sub>2</sub> /SO <sub>2</sub> (molar) | SD  | Measured CO <sub>2</sub> flux (tons/day) | Predicted CO <sub>2</sub> flux            | SD    | Notes/Data Sources  |
| 3  | Popocatepétl                | Mexico                   | 19.02  | −98.62  | 1658                                     | 893  | 8.2   | —  | 7.0 | 9345                                     | —   | 9434  |   |
| 3  | Stromboli                   | Italy                    | 38.79  | 15.21   | 181                                      | 82   | 7.2   | —  | 2.8 | 894                                      | —   | 535   |   |
| 4  | Alu-Dalafilla + Erta Ale    | Ethiopia                 | 13.60  | 40.67   | 64                                       | 24   | 2.3*  | —  | 0.9 | 99                                       | —   | 56    | *Uses Erta Ale comp.; ref. <sup>116</sup>                         |
| 4  | Erebus                      | Antarctica               | −77.53 | 167.17  | 52                                       | 31   | 27.6*   | —  | 4.9 | 983                                      | —   | 612   | *Ref. <sup>117</sup>  |
| 4  | Kilauea                     | USA                      | 19.42  | −155.29 | 5019                                     | 2275 | 0.9*  | —  | 0.2 | 2933                                     | —   | 1578  | *Refs <sup>28,118</sup>   |
| 4  | Nyiragongo + Nyamuragira*   | DR Congo                 | −1.41  | 29.20   | 3533                                     | 2408 | 6.5*  | —  | 1.2 | 15790                                    | —   | 11149 | *Refs <sup>119–121</sup>  |
| 4  | Piton de la Fournaise       | Reunion, France          | −21.23 | 55.71   | 134                                      | 162  | 0.3*  | —  | 0.1 | 28                                       | —   | 34    | *Refs <sup>122</sup> ; Di Muro, pers. comm.                       |
| N.D.   | Marapi                      | Sumatra                  | −0.39  | 100.46  | 34                                       | 34   | 20.5*   | —  | 1.1 | 480                                      | —   | 485   | *This study   |
| “Unmeasured” volcanoes: those for which no CO <sub>2</sub> gas data exist. |                             |                          |        |         |  |      |   |  |     |  |   |       |   |
| A  | B                           | B                        | D      | E       | F  | G    | H   | K  | I   | L = F × H                                | M = F × K                                 | N     | O   |
| Group  | Volcano                     | Country                  | Lat    | Long    | Measured SO <sub>2</sub> flux (tons/day) | SD   | Measured CO <sub>2</sub> /SO <sub>2</sub> (molar) | Predicted CO <sub>2</sub> /SO <sub>2</sub> (molar) | SD  | Measured CO <sub>2</sub> flux            | Predicted CO <sub>2</sub> flux (tons/day) | SD    | Notes/Data Sources  |
| 1  | Anatahan                    | Northern Mariana Islands | 16.35  | 145.67  | 1335                                     | 1867 | —   | 1.2  | 0.5 | —  | 1102                                      | 1607  |   |
| 2  | Aoba                        | Vanuatu                  | −15.40 | 167.83  | 2870                                     | 1229 | —   | 2.5  | 0.7 | —  | 4933                                      | 2524  |   |
| 2  | Bagana                      | Papua New Guinea         | −6.09  | 155.23  | 3779                                     | 886  | —   | 2.4  | 0.7 | —  | 6245                                      | 2335  |   |
| 2  | Barren Island               | India                    | 12.28  | 93.86   | 243                                      | 341  | —   | 2.2*   | 1.3 | —  | 372                                       | 566   | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 2  | Batu Tara + Lewotolo        | Indonesia                | −8.27  | 123.51  | 632                                      | 177  | —   | 2.4*   | 0.7 | —  | 1043                                      | 420   | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 1  | Bulusan                     | Philippines              | 12.77  | 124.05  | 206                                      | 199  | —   | 1.2  | 0.5 | —  | 170                                       | 179   |   |
| 1  | Chiginagak                  | USA- AK                  | 57.14  | −156.99 | 138                                      | 127  | —   | 1.2  | 0.5 | —  | 114                                       | 115   |   |
| 2  | Ebulobo                     | Indonesia/ Nusa          | −8.82  | 121.18  | 86                                       | 63   | —   | 2.6*   | 1.3 | —  | 153                                       | 137   | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 1  | Fuego + Pacaya <sup>§</sup> | Guatemala                | 14.47  | −90.88  | 252                                      | 46   | —   | 1.6*   | 0.8 | —  | 269                                       | 139   | *From the CAVA gas-rock association; Table S1a; Fig. 2a           |
| 2  | Gaua                        | Vanuatu                  | −14.27 | 167.50  | 434                                      | 382  | —   | 2.5*   | 0.7 | —  | 745                                       | 688   | *From the Group 2 global gas-rock association; Table S1d; Fig. 3a |
| 4  | Jebel-at-Tair               | Yemen                    | 15.55  | 41.83   | 103                                      | 295  | —   | 6.2*   | 1.8 | —  | 445                                       | 1527  | *Average on non-arc volcanoes                                     |
| 1  | Kanlaon                     | Philippines              | 10.41  | 123.13  | 70                                       | 182  | —   | 1.2  | 0.5 | —  | 57  | 152   |   |
| 3  | Karangetang                 | Indonesia/ Sulawesi      | 2.78   | 125.40  | 313                                      | 85   | —   | 5.0*   | 1.3 | —  | 1069                                      | 403   | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 1  | Karymsky                    | Russia                   | 54.05  | 159.45  | 912                                      | 250  | —   | 1.2  | 0.5 | —  | 752                                       | 375   |   |
| 2  | Kerinci                     | Indonesia/ Sumatra       | −1.70  | 101.26  | 294                                      | 99   | —   | 2.6*   | 0.8 | —  | 525                                       | 233   | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 1  | Ketoi                       | Russia                   | 47.34  | 152.48  | 139                                      | 151  | —   | 1.2  | 0.5 | —  | 114                                       | 133   |   |
| 1  | Kizimen                     | Russia                   | 55.12  | 160.36  | 711                                      | 1544 | —   | 1.2  | 0.5 | —  | 587                                       | 1297  |   |
| 1  | Korovin                     | USA- AK                  | 52.38  | −174.15 | 198                                      | 160  | —   | 1.2  | 0.5 | —  | 163                                       | 148   |   |
| 2  | Langila                     | Papua New Guinea         | −5.53  | 148.42  | 629                                      | 527  | —   | 2.3*   | 0.7 | —  | 994                                       | 886   | *From the Group 2 global gas-rock association; Table S1d; Fig. 3a |
| 2  | Manam                       | Papua New Guinea         | −4.08  | 145.04  | 1484                                     | 753  | —   | 2.7*   | 0.7 | —  | 2755                                      | 1570  | *From the Group 2 global gas-rock association; Table S1d; Fig. 3a |
| Continued  |                             |                          |        |         |  |      |   |  |     |  |   |       |   |

| Measured volcanoes                         |              |                          |        |         |  |      |   |  |     |  |                                |                            |   |
|--|--------------|--------------------------|--------|---------|--|------|---|--|-----|--|--------------------------------|----------------------------|---|
| A  | B            | B                        | D      | E       | F  | G    | H   | K  | I   | L = F × H                                | M = F × K                      | N                          | O   |
| Group                                      | Volcano      | Country                  | Lat    | Long    | Measured SO <sub>2</sub> flux (tons/day) | SD   | Measured CO <sub>2</sub> /SO <sub>2</sub> (molar) | Predicted CO <sub>2</sub> /SO <sub>2</sub> (molar) | SD  | Measured CO <sub>2</sub> flux (tons/day) | Predicted CO <sub>2</sub> flux | SD                         | Notes/Data Sources  |
| 1  | Michael      | South Sandwich Isl. (UK) | −57.80 | −26.49  | 263                                      | 63   | —   | 1.2  | 0.5 | —  | 217                            | 104                        |   |
| 1  | Montagu      | South Sandwich Isl. (UK) | −58.42 | −26.33  | 142                                      | 179  | —   | 1.2  | 0.5 | —  | 117                            | 155                        |   |
| 2  | Paluweh      | Indonesia/ Nusa          | −8.32  | 121.71  | 60                                       | 65   | —   | 2.6*   | 1.3 | —  | 108                            | 130                        | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 2  | Reventador   | Ecuador                  | −0.08  | −77.66  | 206                                      | 187  | —   | 2.2*   | 0.8 | —  | 304                            | 298                        | *From the SA gas-rock association; Table S1b; Fig. 2d             |
| 3  | Rinjani      | Indonesia/ Lombok        | −8.42  | 116.47  | 74                                       | 131  | —   | 4.3*   | 1.3 | —  | 219                            | 392                        | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 3  | Sangeang Api | Indonesia/ Nusa          | −8.21  | 119.07  | 71                                       | 150  | —   | 4.9*   | 1.3 | —  | 239                            | 508                        | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 1  | Santiaguito  | Guatemala                | 14.76  | −91.55  | 247                                      | 119  | —   | 1.6*   | 0.8 | —  | 271                            | 182                        | *From the CAVA gas-rock association; Table S1a; Fig. 2a           |
| 1  | Sarychev     | Russia                   | 48.08  | 153.21  | 260                                      | 324  | —   | 1.2  | 0.5 | —  | 214                            | 282                        |   |
| 2  | Sinabung     | Indonesia/ Sumatra       | 3.17   | 98.39   | 327                                      | 595  | —   | 2.4*   | 1.3 | —  | 550                            | 1043                       | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 2  | Slamet       | Indonesia/ Java          | −7.24  | 109.21  | 206                                      | 132  | —   | 2.2*   | 1.3 | —  | 311                            | 272                        | *From the Sunda-Banda gas-rock association; Table S1c; Fig. 2g    |
| 2  | Tavurvur     | Papua New Guinea         | −4.24  | 152.21  | 1729                                     | 2535 | —   | 2.6*   | 0.7 | —  | 3091                           | 4607                       | *From the Group 2 global gas-rock association; Table S1d; Fig. 3a |
| 2  | Tinakula     | Solomon back-arc         | −10.38 | 165.80  | 256                                      | 276  | —   | 2.1*   | 0.7 | —  | 370                            | 417                        | *From the Group 2 global gas-rock association; Table S1d; Fig. 3a |
| 1  | Tofua        | Tonga Islands            | −19.75 | −175.07 | 284                                      | 89   | —   | 1.2  | 0.5 | —  | 235                            | 122                        |   |
|  | Tungurahua   | Ecuador                  | −1.47  | −78.44  | 342                                      | 235  | —   | 2.5*   | 0.8 | —  | 588                            | 445                        | *From the SA gas-rock association; Table S1b; Fig. 2d             |
| 2  | Ulawun       | Papua New Guinea         | −5.05  | 151.33  | 630                                      | 581  | —   | 2.4*   | 0.7 | —  | 1040                           | 1005                       | *From the Group 2 global gas-rock association; Table S1d; Fig. 3a |
| 1  | Veniaminof   | USA- AK                  | 56.17  | −159.38 | 255                                      | 214  | —   | 1.2  | 0.5 | —  | 211                            | 197                        |   |
|  |              |                          |        |         | Measured SO <sub>2</sub> flux            | SD   |   |  |     | Measured CO <sub>2</sub> flux            | Predicted CO <sub>2</sub> flux | Total CO <sub>2</sub> flux |   |
| GRAND TOTAL (Mt/yr, 10 <sup>9</sup> kg/yr) |              |                          |        |         | 23                                       | 15   |   |  |     | 27.4 ± 3.6                               | 11.4 ± 1.4                     | 38.7 ± 2.9                 |   |
| GRAND TOTAL (10 <sup>12</sup> mol/yr)      |              |                          |        |         | 0.36                                     | 0.23 |   |  |     | 0.62 ± 0.08                              | 0.26 ± 0.02                    | 0.88 ± 0.06                |   |

**Table 1.** Gas composition and fluxes for the 91 strongest SO<sub>2</sub> volcanic gas sources in 2005–2015 worldwide (from Carn *et al.*, 2017). The quoted SO<sub>2</sub> fluxes (column F) are 2005–2015 averages (and standard deviation, SD) taken from the compilation of ref.<sup>30</sup>. The “measured volcanoes” list includes those volcanoes for which SO<sub>2</sub> flux and gas composition molar CO<sub>2</sub>/SO<sub>2</sub> ratios have both been measured. Each volcano is assigned to a given Group (1–4) (column A) based on the original categorization of ref.<sup>36</sup> (non-arc volcanoes are assigned to Group 4). Unless indicated (see references in column O), the measured CO<sub>2</sub>/SO<sub>2</sub> ratios (column H) are from ref.<sup>36</sup>. For these strongly degassing volcanoes, we assume total S (S<sub>T</sub>; quoted in 36) equals to SO<sub>2</sub>; SO<sub>2</sub> satellite detection for all these volcanoes implies high-emission temperatures and limited or no interaction with hydrothermal system (and thus trivial reduced S species, such as H<sub>2</sub>S). Marapi volcano in Sumatra is an exception because of its hydrothermal signature (high CO<sub>2</sub>/SO<sub>2</sub>, high H<sub>2</sub>S) and is not assigned to any specific group (N.D. = not determined). In cases where combined emissions from two volcanoes are listed in the original dataset<sup>30</sup> (see volcanoes labelled with superscripts \* and § in column B), due to insufficient spatial OMI resolution, a weighted average was calculated from the available volcanic gas information for the 2 where possible. Otherwise, equal<sup>§</sup>

gas contribution was assumed for the two volcanoes. The measured  $\text{CO}_2$  flux (column L) is calculated from the product of F by H (the quoted standard deviations in column N are based on propagation of the respective errors). The “unmeasured volcanoes” list includes volcanoes for which gas  $\text{CO}_2/\text{S}_\text{T}$  data are unavailable. Thirteen of such “unmeasured” (for gas) volcanoes are sited in arc segments with no subducted carbonate-rich lithologies at the respective trenches, and are therefore assigned to Group 1 (e.g., they are assigned the mean  $\text{CO}_2/\text{S}_\text{T}$  ratio of  $1.2 \pm 0.5$  of Group 1 volcanoes; see Table S1). For the remaining volcanoes, we predict the time-averaged  $\text{CO}_2/\text{S}_\text{T}$  (here considered as equivalent to  $\text{CO}_2/\text{SO}_2$ ; column K) from the averaged (mean) trace-element composition of the corresponding volcanic rocks (Table S1) and the individual arc/global arc  $\text{CO}_2/\text{S}_\text{T}$  vs. Ba/La associations (see Figs 2 and 3). Uncertainty in the predicted  $\text{CO}_2/\text{S}_\text{T}$  ratios (column I) is the confidence interval calculated from the regression line and one standard deviation about the regression, and incorporates uncertainty/variability in “measured” gas  $\text{CO}_2/\text{S}_\text{T}$  ratios (average uncertainty at  $1\sigma$ , ~26%) and whole-rock Ba/La ratios (average uncertainty at  $1\sigma$ , ~16%) (see Table S1). Column O references the supplementary table (Table S1) detailing the specific  $\text{CO}_2/\text{S}_\text{T}$  vs. Ba/La relation used. The  $\text{SO}_2$  flux GRAND TOTAL of  $23 \pm 15$  Mt/yr is from ref.<sup>32</sup>. The GRAND TOTAL for measured, predicted and total  $\text{CO}_2$  flux is obtained by applying Monte Carlo method to the  $\text{CO}_2$  datasets of columns L, M and L + M, respectively. For each of the three datasets, 100 simulations are considered. In each simulation, the  $\text{CO}_2$  flux for each volcano is left to vary randomly within its mean  $\pm$  SD value, and the resulting  $\text{CO}_2$  fluxes are summed up. The procedure is repeated 100 times, yielding 100 random-generated sums. The GRANDTOTAL values quoted in the tables are ranges (mean  $\pm$  1 SD) of 70% of the three populations of random-generated sums (e.g., the 15% outliers on each end of the populations are omitted). With this procedure, the global volcanic  $\text{CO}_2$  flux is assessed at  $38.7 \pm 2.9$  Mt/yr,  $\sim 11.4 \pm 1.4$  Mt/yr of which is estimated for the 34 “unmeasured” volcanoes (those with no measured gas data available).

into  $\text{CO}_2$  fluxes (Table 1). The remaining 34 volcanoes, however, have so far been impossible to characterise for gas composition, owing to their remoteness and/or poor accessibility, leaving their  $\text{CO}_2$  fluxes unconstrained.

Here, we explore an alternative approach of indirectly inferring the  $\text{CO}_2/\text{S}_\text{T}$  ratio signature of these “unmeasured” volcanoes, and ultimately their  $\text{CO}_2$  flux, based on the (far more commonly measured) trace element compositions of their erupted volcanic rocks. Volcanic arc gas  $\text{CO}_2/\text{S}_\text{T}$  ratios and whole-rock trace element ratios (e.g., Ba/La or Sr/Nd ratios) are globally linked<sup>36</sup>, as both volatiles and fluid/melt-mobile elements (e.g., Ba and Sr) are sourced from fluids delivered from dehydration/melting of subducting slab sediments and altered ocean crust<sup>37–42</sup>. Based on their gas vs. whole-rock associations, arc volcanoes cluster into three Groups<sup>36</sup>. Group 1, which includes C-poor arc volcanoes (gas  $\text{CO}_2/\text{S}_\text{T}$  ratios  $\leq 2$ ), are thought<sup>36</sup> to be sourced by a mantle wedge source contaminated by C-poor slab fluids (derived from either terrigenous sediments or altered oceanic crust). Group 2 volcanoes are assumed to inherit their C-richer ( $2 \leq \text{CO}_2/\text{S}_\text{T}$  ratios  $\leq 4$ ) gas composition from incorporation into the mantle wedge of slab fluids derived from melting of carbonated sediments. Group 3 ( $\text{CO}_2/\text{S}_\text{T}$  ratios  $> 4$ ), finally, includes C-rich arc gases, supporting the involvement of an additional crustal C contribution (de-carbonation/assimilation of upper crustal limestones<sup>43,44</sup>).

We here establish systematic gas vs. rock relationships at the scale of individual arc segments and/or groups of volcanoes. These relationships, once set, allow us to predict the  $\text{CO}_2/\text{S}_\text{T}$  ratio for any volcano for which trace-element whole-rock information (but not gas composition) is available. Ultimately, using these predicted  $\text{CO}_2/\text{S}_\text{T}$  ratios in tandem with available  $\text{SO}_2$  flux information<sup>30</sup>, we derive  $\text{CO}_2$  fluxes for all current top-degassing volcanoes and, by summation, a refined inventory of decadal (2005–2015) global  $\text{CO}_2$  emissions from subaerial volcanism.

## Results

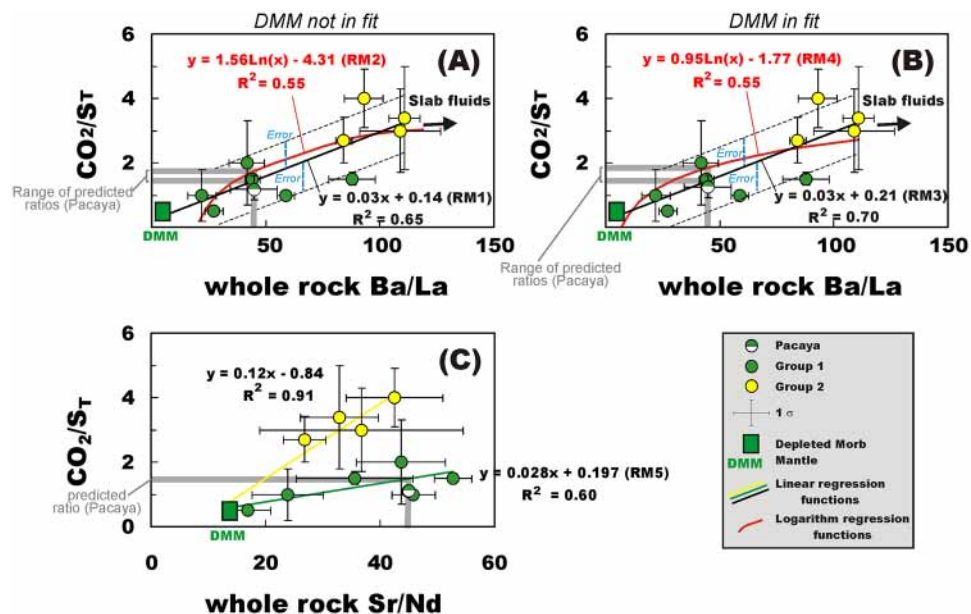
**$\text{CO}_2$  fluxes for the Earth’s best-studied volcanoes.** Roughly ~62% of the 91 strongest volcanic  $\text{SO}_2$  sources globally<sup>30</sup> have been characterised for both  $\text{SO}_2$  flux and (episodically) for volcanic gas compositions (Table 1).  $\text{CO}_2$  fluxes are thus obtained (see “Methods”) by pairing the OMI-based time-averaged 2005–2015  $\text{SO}_2$  fluxes<sup>30</sup> with the characteristic (mean)  $\text{CO}_2/\text{SO}_2$  ratios in the corresponding high-temperature magmatic gases (data from ref.<sup>36</sup> unless otherwise noted). The so-derived  $\text{CO}_2$  fluxes (Table 1) range from 28 to 15,800 tons/day, and are in reasonable agreement (typically within a factor  $\leq 40\%$ ) with the  $\text{CO}_2$  fluxes estimated using ground-based  $\text{SO}_2$  flux measurements<sup>11,15</sup>. We estimate the cumulative  $\text{CO}_2$  flux from the 57 volcanic sources with “measured” gas compositions by applying a Monte Carlo method (see Table 1) to the dataset. The obtained cumulative “measured” flux is  $27.4 \pm 3.6$  Mt/yr (or  $0.62 \pm 0.08 \cdot 10^{12}$  mol/yr).

**Matching gas and whole-rock trace element compositions.** Thirty-four top-ranking volcanic  $\text{SO}_2$  sources do not have gas compositional records (Table 1). We hereafter refer to such volcanoes without  $\text{CO}_2/\text{S}_\text{T}$  information as “unmeasured” volcanoes.

We thus explore a methodology to predict the characteristic volcanic gas  $\text{CO}_2/\text{S}_\text{T}$  ratio of each of these 34 “unmeasured” volcanoes using their averaged trace-element volcanic rock composition (Table S1). Gas  $\text{CO}_2/\text{S}_\text{T}$  ratios in arc volcanoes exhibit systematic global relationships with slab fluid trace-element proxies (e.g., Ba/La or Sr/Nd ratios) in the corresponding whole-rocks, which are interpreted<sup>36</sup> as resulting from a common  $\text{CO}_2$ -Ba-Sr derivation from melting of subducted sediments in the slab<sup>40</sup> (variably enriched in  $\text{CO}_2$ ; ref.<sup>42</sup>). These relationships, once set at the scale of individual arc segments (Figs 1 and 2) or volcano Groups (Fig. 3), can now be used to infer the representative volcanic gas  $\text{CO}_2/\text{S}_\text{T}$  ratio signature of the 34 “unmeasured” volcanoes (Tables 1 and S1).

The procedure is illustrated in Fig. 1 and Table 2 for Pacaya volcano as an example (see “Methods”). The initial step involves establishing a  $\text{CO}_2/\text{S}_\text{T}$  vs. Ba/La relationship using data for volcanoes for which both gas and



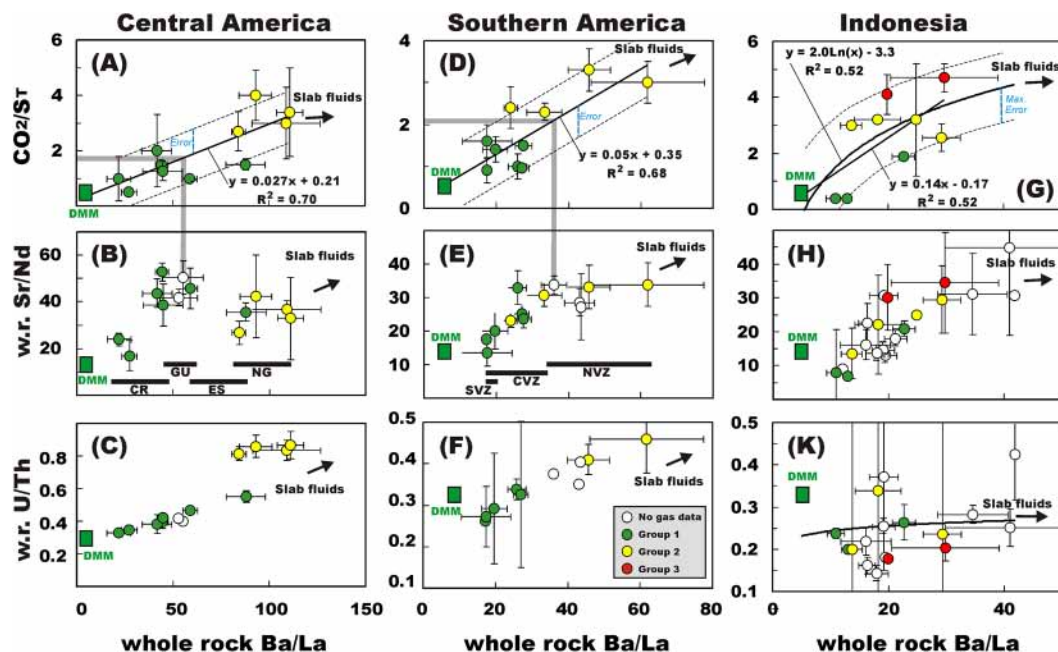


**Figure 1.** The proxy approach for estimating the  $\text{CO}_2/\text{S}_\text{T}$  ratio for “unmeasured” volcanoes (i.e., those for which no gas data exist), based on the averaged trace-element composition of the corresponding volcanic rocks. The procedure is illustrated for Pacaya volcano in Guatemala. Firstly, the association between  $\text{CO}_2/\text{S}_\text{T}$  ratios in volcanic gases (corresponding to  $\text{CO}_2/\text{SO}_2$  gas ratios in the high-temperature systems studied here) and whole-rock Ba/La ratios is established at the scale of the Central American Volcanic Arc (CAVA) segments, using data for volcanoes for which both gas and trace element data are available (see Table S1a). Secondly, the gas vs. trace-element trend is fitted via either a linear or logarithm best-fit regression function. Tests made excluding (panel A) or including (panel B) the compositional point of the Depleted Mid-ocean ridge Mantle (DMM; refs<sup>123,124</sup>) in the data-fitting found that the second option systematically led to the best-data fits (see Table 2). Finally, the preferred regression model function (RM3 in the Pacaya example; see panel B and Table 2) is used to calculate a “predicted” gas  $\text{CO}_2/\text{SO}_2$  from available Ba/La data for Pacaya whole-rocks (uncertainty is estimated from confidence interval at one standard deviation on the regression). Our inferred gas  $\text{CO}_2/\text{S}_\text{T}$  ratio ( $1.4 \pm 0.75$ ; Table 2) is well within the magmatic gas range ( $\text{CO}_2/\text{SO}_2$  ratio of  $1.1 \pm 1.0$ ) measured during recent plume observations<sup>46</sup>. A similar  $\text{CO}_2/\text{S}_\text{T}$  ratio (see Table 2) is predicted using the CAVA gas vs. Sr/Nd ratio association (panel C). In this plot, the yellow and green dashed lines are the linear best-fit regression lines for Group 1 and 2 sub-populations, respectively.

trace element data are available (for the specific Pacaya example, we use gas/whole-rock information for Central American volcanoes, see Table S1a and Fig. 1). As in previous work<sup>36</sup>, the representative  $\text{CO}_2/\text{S}_\text{T}$  ratios used in Fig. 1 (listed in Table 1 and S1a) are obtained by averaging available results for high-temperature gas samples, in the attempt to reduce the effect of secondary processes (e.g., magmatic S scrubbing during gas-water-rock reactions<sup>45</sup>) that become substantial at hydrothermal (temperature  $< 400^\circ\text{C}$ ) conditions. Secondly, regression analysis is used to fit the gas vs. trace-element association via either a (i) linear or (ii) logarithmic regression model (Fig. 1; see “Methods”). We focus on the two regression models based on the assumption that linear/logarithmic functions best describe depleted mantle (DMM)-slab fluid mixing in a  $\text{CO}_2/\text{S}_\text{T}$  ratio vs. Ba/La (or Sr/Nd) compositional field<sup>36</sup>. Finally, the adopted regression function is used to derive a “predicted” gas  $\text{CO}_2/\text{S}_\text{T}$  from available Ba/La whole rock data (Fig. 1). In the specific Pacaya example (Fig. 1 and Table 2), using a linear regression to fit the volcanic gas and DMM data-points (our RM3 regression model, see “Methods” and Table S1), the “predicted” gas  $\text{CO}_2/\text{SO}_2$  ratio is  $1.4 \pm 0.75$ , well within the magmatic gas range ( $\text{CO}_2/\text{SO}_2$  ratio of  $1.1 \pm 1.0$ ) recently determined<sup>46</sup> from plume measurements (Fig. 1).

**$\text{CO}_2/\text{S}_\text{T}$  ratios from individual-arc gas vs. trace-element relationships.** Gas vs. rock (trace element composition) associations are initially analysed at the scale of individual arc segments, in the assumption that, at such regional scales, sources and transport pathways of volatiles and trace elements are relatively uniform. In truth, intra-arc variations in thickness, age, thermal properties and composition of the slab and overlying plate<sup>47</sup>, and in the composition of subducted sediments<sup>42</sup>, are large enough to impact the mechanisms of magma generation, and thus impart regional trends in volatile<sup>48</sup> and trace element<sup>49</sup> signatures of erupted magmas. Nonetheless, it is on these individual-arc trends that we rely below. Three arc segments have enough volcanoes measured for both gases and rocks to allow reliable gas vs. rock associations to be established (Fig. 2).

The Central American Volcanic Arc (CAVA)  $\text{CO}_2/\text{S}_\text{T}$  vs. Ba/La relationship, obtained from results listed in Table S1a, is illustrated in Figs 1 and 2a. The systematic along-arc trace-element patterns in CAVA volcanic rocks<sup>49</sup> (Fig. 2b,c) originate from changes in geometry, age, thermal regime and extent of serpentinization of the subducting Cocos plate slab<sup>50</sup>. As more recently found<sup>36,51</sup>, such trace-element variations correlate with those of  $\text{CO}_2/\text{S}_\text{T}$  ratios in high-temperature magmatic CAVA gases. These correlations (e.g., Figs 1 and 2a) have been explained<sup>36,51</sup>

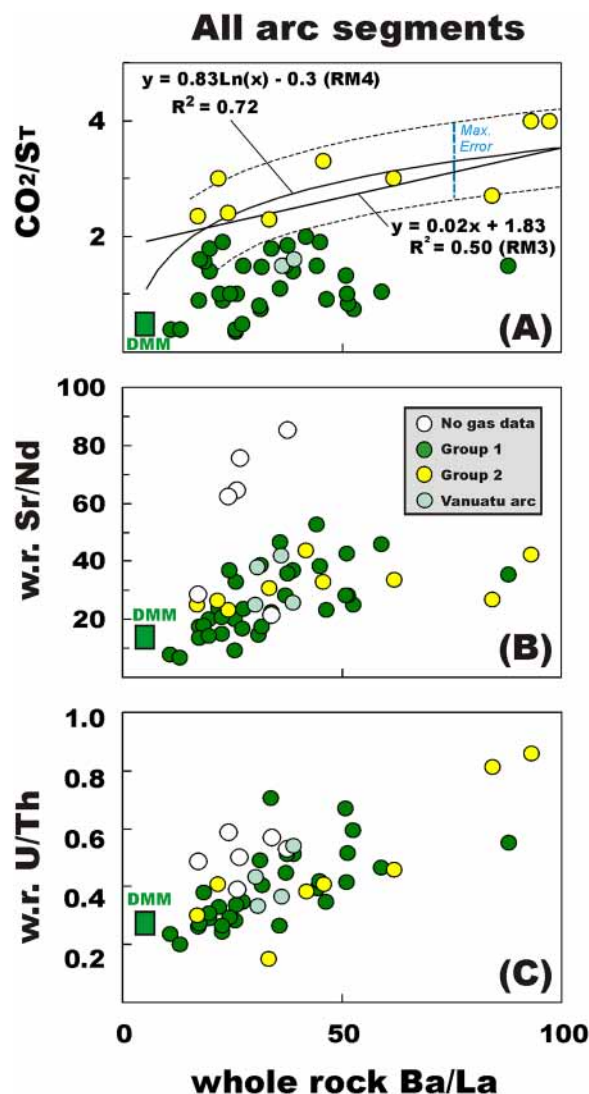


**Figure 2.** Scatter plots of mean Ba/La whole-rock ratios vs. volcanic gas CO<sub>2</sub>/S<sub>T</sub> ratios (panels A, D and G), whole-rock Sr/Nd ratios (panels B, E and H) and whole-rock U/Th ratios (panels C, F and K) for three arc segments (left, Central America; middle, Southern America; right Sunda-Banda arc in Indonesia). Each symbol corresponds to an individual volcano for which gas and trace element information is simultaneously available (see Tables S1a–c for the list of volcanoes, compositions used, and data sources). The gas vs. trace element correlations are explained in terms of mixing between a C-Ba-Sr-U-poor Depleted Mid-ocean ridge Mantle (DMM) and C-Ba-Sr-U-rich slab fluids. C-poor arc volcanoes (Group 1, in green) plot close to the DMM, while Group 2 arc volcanoes (in yellow) are C-enriched to larger slab fluid influx. The even more C-rich signature of Group 3 arc volcanoes (in red) may reflect some addition of crustal carbon<sup>36</sup>. For each arc segment, panels A, D, and G show the best-fit regression functions used to predict the volcanic gas CO<sub>2</sub>/S<sub>T</sub> ratios for “unmeasured” volcanoes (open symbols; see Tables 1 and S1b–d). The grey lines illustrate (for two “unmeasured” volcano examples) the procedure used to convert whole-rock Ba/La ratios into gas CO<sub>2</sub>/S<sub>T</sub> ratios, using the equations of the best-fit regression lines.

| Measured CO <sub>2</sub> /SO <sub>2</sub> (molar) | Predicted CO <sub>2</sub> /S <sub>T</sub> (linear regression model RM1) | Predicted CO <sub>2</sub> /S <sub>T</sub> (logarithm regression model RM2) | Predicted CO <sub>2</sub> /S <sub>T</sub> (linear regression model RM3) | Predicted CO <sub>2</sub> /S <sub>T</sub> (logarithm regression model RM4) | Predicted CO <sub>2</sub> /S <sub>T</sub> (linear regression model RM5) |
|---|---|--|---|--|---|
| 1.1 ± 0.9   | 1.4 ± 0.75  | 1.6 ± 0.8  | 1.4 ± 0.75  | 2.0 ± 0.8  | 1.3 ± 0.75  |

**Table 2.** Comparison between measured<sup>46</sup> and predicted (this work) volcanic gas CO<sub>2</sub>/S<sub>T</sub> ratios in the Pacaya magmatic gases. At the high-T magmatic gas conditions explored here, total S (S<sub>T</sub>) corresponds to SO<sub>2</sub>. The predicted CO<sub>2</sub>/S<sub>T</sub> ratios are obtained from the mean Ba/La ratio (or Sr/Nd; see RM5) in Pacaya whole-rocks using the regression functions through the CO<sub>2</sub>/S<sub>T</sub> vs. Ba/La (or Sr/Nd; see RM5) association for CAVA volcanoes (dataset listed in Table S1a). Five distinct regression functions are tested, being illustrated (with their corresponding equations and regression coefficients) in Fig. 1. RM1 and RM2 (Fig. 1a) use linear and logarithmic regression models, respectively, and do not include the composition of the Depleted mid-ocean ridge Mantle in the fit. Regression models RM3 and RM4 (Fig. 1b) are, respectively, linear and logarithmic, and the composition of the Depleted mid-ocean ridge Mantle is included in the fit. Regression models RM5 (Fig. 1c) uses linear regression functions through the CO<sub>2</sub>/S<sub>T</sub> vs. Sr/Nd association for Group 1 CAVA volcanoes. The linear regression model RM3 yields the highest regression coefficient ( $R^2 = 0.7$ ; see Fig. 1b), and is thus adopted here.

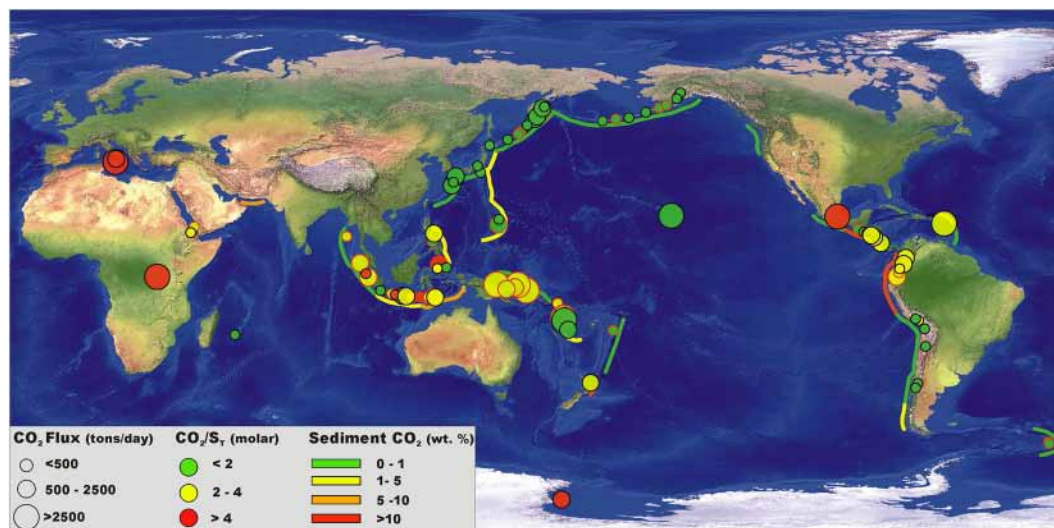
as resulting from the variable addition of C-Ba-Sr-rich fluids issuing from melting of limestone-bearing slab sediments, with the highest slab-fluid influx being observed in Nicaragua<sup>52</sup>, where magmatic gases consistently have C-rich (Group 2) affinity (Fig. 2a). In Costa Rica and El Salvador, magmatic gases are typically C-poorer<sup>36,51</sup> (Group 1), in line with the lower slab affinity (and more depleted mantle-like signature) of trace-element ratios (Fig. 2). All the CAVA volcanic SO<sub>2</sub> emitters of Table 1 have been measured for gas composition (at least for their CO<sub>2</sub>/S<sub>T</sub> ratio), except for Guatemalan volcanoes Fuego and Santa Maria. We use the CAVA CO<sub>2</sub>/S<sub>T</sub> vs. Ba/La association (of Fig. 2a) to fill this gap of knowledge. Using the RM3 regression model in tandem with mean whole-rock Ba/La ratios (Table S1a and Fig. 2a), we infer CO<sub>2</sub>/S<sub>T</sub> ratios of respectively  $1.7 \pm 0.75$  (Fuego) and  $1.6 \pm 0.75$  (Santa Maria).



**Figure 3.** Scatter plots of mean Ba/La whole-rock ratios vs. (A) volcanic gas  $\text{CO}_2/\text{S}_\text{T}$  ratios, (B) whole-rock Sr/Nd ratios and (C) whole-rock U/Th ratios (panels C, F and K) for Group 1 volcanoes (green, see Table S1d) and Group 2 volcanoes (yellow, see Table S1e) globally. Each symbol corresponds to an individual arc volcano for which gas and trace element information is simultaneously available (see Tables S1d–e for the list of volcanoes, compositions used, and data sources). Volcanoes with no gas compositional information are shown as open circles. The Vanuatu arc volcanoes are plotted in light green. The best-fit regression functions through the populations of Group 1 and Group 2 volcanoes are separately illustrated. Group 1 volcanoes exhibit little change in gas  $\text{CO}_2/\text{S}_\text{T}$  ratios on increasing Ba/La. Their mean  $\text{CO}_2/\text{S}_\text{T}$  ratio of  $1.2 \pm 0.5$  (see Table S1d) is thus adopted for all the “unmeasured” (for gas) Group 1 volcanoes (Table 1). For the “unmeasured” Group 2 volcanoes, we average the predicted volcanic gas  $\text{CO}_2/\text{S}_\text{T}$  ratios obtained from regression functions RM3 and RM4 (see Tables 1 and S1e).

Our compilation (Table 1) shows that volcanic gas  $\text{CO}_2/\text{S}_\text{T}$  data are available for the majority of the volcanic  $\text{SO}_2$  emitters in the Northern (NVZ), Central (CVZ) and Southern (SVZ) Volcanic Zones<sup>53</sup> of the Andes (Southern America). Very limited gas information is available<sup>54</sup> for Ecuadorian volcanoes, however, and here we use the  $\text{CO}_2/\text{S}_\text{T}$  vs. Ba/La association (for South-America: Fig. 2d) to fill this knowledge gap. In the Andes, there is documented evidence in the literature for large along-arc variations in volcanic rock trace-element geochemistry<sup>55–58</sup>. Our partial whole-rock dataset, based on the subpopulation of Andean volcanoes listed in Table S1b, demonstrates an overall south-to-north increase in trace-element slab-fluid proxies (Ba/La, Sr/Nd and U/Th; Fig. 2e,f), from Copahue volcano in Argentina (SVZ) to Nevado de Ruiz in Colombia (NVZ). Importantly, the along-arc variations in the volcanic gas  $\text{CO}_2/\text{S}_\text{T}$  ratio scale well with the trace-element variation patterns (Fig. 2d), again suggesting common source processes. The trace-element signature of the three most actively degassing volcanoes today in Ecuador, Tungurahua<sup>59</sup>, El Reventador<sup>60</sup> and Cotopaxi<sup>61</sup> (the latter not appearing in the 91 list of top degassing volcanoes<sup>30</sup>), places Ecuadorian magmatism in an intermediate position between Colombian volcanoes in the NVZ (the richest in Ba and Sr, but also  $\text{CO}_2$ ; Fig. 2d) and intermediate C-rich Peruvian volcanoes<sup>62</sup>

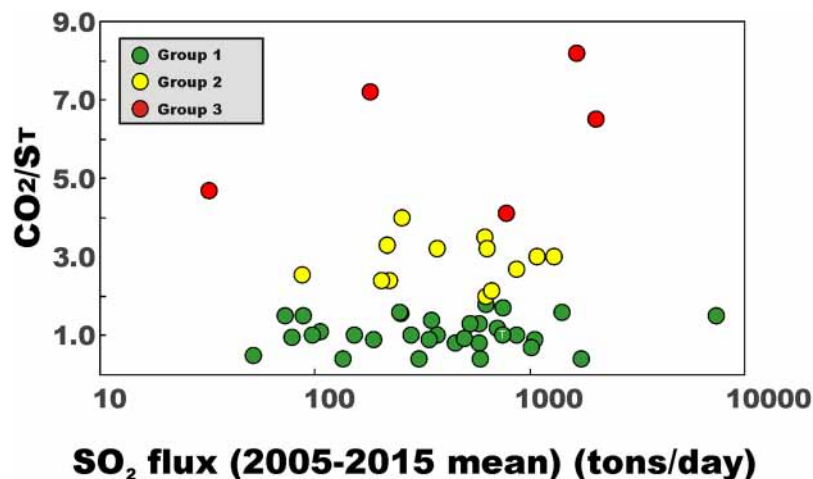




**Figure 4.** Global map illustrating the location of the 91 strongest volcanic CO<sub>2</sub> emitters (data from Table 1). CO<sub>2</sub> flux information for both “measured” (circles with black borders) and “unmeasured” (circles with red borders) volcanoes is shown. Dimension of the symbols is proportional to CO<sub>2</sub> flux, with color fill reflecting the CO<sub>2</sub>/S<sub>T</sub> ratio (see legend). Trenches are differently colored depending on CO<sub>2</sub> bulk concentration in the trench sediments (data from ref.<sup>42</sup>). The map shows that the most strongly CO<sub>2</sub> degassing volcanoes are clustered in tropic to sub-tropical regions such as the Vanuatu-Papua New Guinea arc segments, in Central America, Southern American (Northern Volcanic Zone), and in the Lesser Antilles, in addition to Italy (Etna), Congo (Nyirangongo + Nyamuragira) and Hawaii (Kilauea). Volcanic CO<sub>2</sub> fluxes are typically lower in higher latitude volcanic regions such as in the Aleutians-Kamchatka-Kuriles and in the South-Sandwich Islands, where no carbonate-rich lithologies are subducted at the trenches. The map was generated using the open source QGIS software (available at <https://www.qgis.org/it/site/>) (Copyright © 2019 AIUPPA. Permission is granted to copy, distribute and/or modify this document under the terms of the GNU Free Documentation License, Version 1.3 or any later version published by the Free Software Foundation; with no Invariant Sections, no Front-Cover Texts, and no Back-Cover Texts. A copy of the license is included in the section entitled “GNU Free Documentation License”). The base map is a relief and bathymetry Raster called “Natural Earth II with Shaded Relief and Water” file #NE2\_HR\_LC\_SR\_W.tif (Made with Natural Earth. Free vector and raster map data @ [naturalearthdata.com](http://naturalearthdata.com)). As for the shaded relief, we use the CleanTOPO2 layer, a modified SRTM30 Plus World Elevation Data also edited by Tom Patterson, US National Park Service. The original source data is from ref.<sup>125</sup>.

further to the south (in the CVZ). The mean Ba/La ratios, combined with the CO<sub>2</sub>/S<sub>T</sub> vs. Ba/La linear regression model displayed in Fig. 2d, constrain the CO<sub>2</sub>/S<sub>T</sub> ratio for Tungurahua and El Reventador at  $2.5 \pm 0.8$  and  $2.2 \pm 0.8$ , respectively (see Table 1 and S1b). A consistent CO<sub>2</sub>/S<sub>T</sub> ratio is inferred for Cotopaxi ( $2.5 \pm 0.8$ ).

The case of Indonesia, which includes the Sunda-Banda and Sangihe-Halmahera arc segments, is particularly problematic (Fig. 2g–k). The large along- and within-arc variations in crustal<sup>63</sup> and slab<sup>64</sup> structures, combined with heterogeneities in the sedimentary slab input<sup>42</sup> (Fig. 4), make it difficult to characterize regional trends in volatile sources. In the Java sector of the Sunda arc, the respective roles of crust and slab in controlling rock<sup>65</sup> and gas<sup>66</sup> geochemistry are widely debated, with some authors stressing the importance of upper plate assimilation<sup>67,68</sup> and others emphasising a slab control<sup>69–71</sup>. The Group 3 signature<sup>36</sup> of Merapi and Bromo (Fig. 2g) supports involvement of crustal carbon in Central Java<sup>72</sup>. South-to-north along-arc trends in gas <sup>3</sup>He/<sup>4</sup>He (decreasing) and CO<sub>2</sub>/<sup>3</sup>He (increasing) ratios<sup>66</sup> suggest a crustal volatile contribution is also likely in Sumatra, where the crust is especially thick and limestones widely exposed<sup>63,67</sup>. In contrast, crustal assimilation is supposedly minor (if any) in other sectors, including west and east-Java<sup>65</sup>, Nusa<sup>69,73</sup>, Banda<sup>74</sup> and Halmahera<sup>33</sup>. In these segments of the Sunda-Banda and Sangihe-Halmahera arcs<sup>75</sup>, along-arc variations in He-C isotopes<sup>66,76,77</sup>, and the sparse high-temperature gas information, suggest variable C delivery from the slab, and thus coexistence of Group 1 and 2 volcanism (Fig. 2g). This is not unexpected, in view of the C heterogeneity in subducted sediments, from terrigenous and C-poor (Sumatra-Java) to pelagic and C-richer (Nusa, east Sunda)<sup>42</sup> (Fig. 4). The diverse volatile sources that are possibly involved, in addition to the paucity of gas data, create scatter in CO<sub>2</sub>/S<sub>T</sub> vs. Ba/La (Fig. 2g). Only 9 Indonesian volcanoes have been measured for both whole-rock trace element composition and (high-temperature) magmatic gas composition (Table S1c). These CO<sub>2</sub>/S<sub>T</sub> vs. Ba/La data can be fitted by either a linear (RM3) or logarithm (RM4) regression model with identical regression coefficients ( $R^2 = 0.52$ ; Fig. 2g). We therefore infer the CO<sub>2</sub>/S<sub>T</sub> ratio signature of the “unmeasured” Indonesian volcanoes (Table 1) by averaging the output of the two regression models (Table S1c). The low regression coefficients (Fig. 2g) imply the inferred CO<sub>2</sub>/S<sub>T</sub> ratios should be treated with caution, as they require validation/refinement with an improved (more than 9 data-points) gas vs. trace element relationship. We caution, in particular, that the predicted CO<sub>2</sub>/S<sub>T</sub> ratios (Table 1) may either over-estimate (for Group 1 volcanoes) or under-estimate (for Group 3 volcanoes) by a factor ~1.3 (the max error in Fig. 2g) the real volcanic gas CO<sub>2</sub>/S<sub>T</sub> ratios of “unmeasured” Indonesian volcanoes.



**Figure 5.** Scatter plot exploring the relationship between the  $\text{SO}_2$  flux (2005–2015 mean; data from ref.<sup>33</sup>) and the volcanic gas  $\text{CO}_2/\text{S}_T$  ratio for the population of “measured” volcanoes in Table 1. For Turrialba + Poas (T), we plot the best-guess estimate for the magmatic gas  $\text{CO}_2/\text{S}_T$  ratio for Turrialba volcano (data from 28 top-ranking volcanic point sources of  $\text{SO}_2$  (left) and  $\text{CO}_2$  (right) during 2005–2015. Data are from Table 1.  $\text{SO}_2$  fluxes are 2005–2015 means from ref.<sup>30</sup>. The  $\text{CO}_2$  fluxes are calculated from  $\text{SO}_2$  using measured or predicted  $\text{CO}_2/\text{SO}_2$  ratios (see Table 1). Different volcano groups are identified by different colours. The global  $\text{CO}_2$  budget is dominated by  $\text{CO}_2$ -rich Group 2–3 arc volcanoes. Two rift volcanoes (Nyiragongo and Nyamuragira) and one within-plate (WP) volcano (Kilauea) appears in the top-10 list of  $\text{CO}_2$  emitting volcanoes.

**$\text{CO}_2/\text{S}_T$  ratios from Group-based gas vs. trace element relationships.** Several of the “unmeasured” (for gas) volcanoes in Table 1 are sited in arc segments for which insufficient gas/rock information is currently available to establish individual-arc associations (as those analysed in Fig. 2). In order to derive information on their  $\text{CO}_2/\text{SO}_2$  ratio gas signature, we use the global relationship between  $\text{CO}_2/\text{S}_T$  and Ba/La in Groups 1–2 volcanoes (ref.<sup>36</sup>) (Fig. 3).

The majority of the remaining “unmeasured” (for gas) volcanoes in Table 1 are sited in arc segments for which available deep sea drill holes point to the lack of C-rich lithologies (limestones) in the subducted sediment succession<sup>42</sup> (Fig. 4). Trench sediments poor in C have been identified in the segment of the Pacific Ring of Fire (Fig. 4) that stretches from Aleutians-Kuril-Kamchatka to the N/NW to Marianas/Japan/Philippines further south (10 “unmeasured” volcanoes in total – see Table 1). Where high-temperature gas information is available, a  $\text{CO}_2$ -poor (Group 1) signature of volcanic gases<sup>36</sup> has typically been observed in such carbonate-poor trenches (Fig. 4), matching well the small sedimentary slab C input<sup>42</sup>. Sediments are similarly C-poor (e.g., prevailingly terrigenous and biosiliceous<sup>42</sup>) in the Tonga and South Sandwich arcs (3 “unmeasured” volcanoes; Fig. 4). We therefore assign to Group 1 all the “unmeasured” (for gas) arc volcanoes fed by carbonate-poor trenches. Group 1 volcanoes exhibit little change in gas  $\text{CO}_2/\text{S}_T$  ratios with increasing Ba/La (Fig. 3a). This implies either (i) limited C delivery from the slab in the absence of carbonated sediments (e.g., that fluids/melts delivered by terrigenous sediments, altered oceanic crust and/or serpentinite are not major C sources<sup>36</sup>), or (ii) that slab C and S are added to the mantle wedge in 1:1 to 4:1 proportions at most (Group 1 volcanoes typically have  $\text{CO}_2/\text{S}_T$  ratios ~3–4 times higher than the DDM). The lack of dependence on Ba/La (Fig. 3a) means that we can prudently use the measured Group 1  $\text{CO}_2/\text{S}_T$  ratio average ( $1.2 \pm 0.5$ ; see Table S1d) for all the “unmeasured” (for gas) Group 1 volcanoes in Table 1.

Group 2 volcanoes are, by definition<sup>36</sup>, those having  $\text{CaCO}_3$ -rich sediments in their trenches. These volcanoes typically have more C-rich volcanic gas composition ( $\text{CO}_2/\text{S}_T$  ratio  $>2$  but  $\leq 4$ ) and exhibit stronger, steeper correlation between gas  $\text{CO}_2/\text{S}_T$  and trace element ratios (Fig. 3a). These Group 2 volcanoes are located in high biological productivity zones close to the tropics, where sediments are increasingly biogenic in nature and/or where seafloor is shallow enough (above the calcite compensation depth, CCD) to support carbonate deposition<sup>42</sup> (Fig. 4). Of the few remaining “unmeasured” (for gas) volcanoes in Table 1, those in the Papua New Guinea-Solomon-Vanuatu arc segment are thus potential candidates for Group 2. The Papua New Guinea-Solomon arc sectors (Fig. 4) are a particular challenge because no gas samples are available, and no deep sea drill holes have been placed in the seafloor of the Solomon Sea, seaward of their trenches. Likewise, there are few relevant piston cores to provide any seafloor samples. Our inferences are thus based on seafloor depth, assumptions about the regional CCD, and drill sites in other, nearby southwest Pacific marginal seas. At DSDP Site 63, in the East Caroline Basin north of New Britain, carbonate lithologies were encountered throughout the entire section, from the Quaternary to the middle Oligocene basaltic basement<sup>78</sup>. This site, at 4472 m water depth, has thus been above the CCD over its entire history. Similarly, drilling at DSDP 287 (4653 m water depth), in the Coral Sea south of Papua New Guinea and east of the Solomon Islands, intercepted abundant carbonate lithologies through most of the sedimentary section to its lower Eocene basement<sup>79</sup>. Given that the water depths of the Solomon Sea are predominantly  $<4500$  m seaward of the New Britain, Solomon and Northern Vanuatu trenches, we expect this seafloor to have been above the CCD for much of its history as well, and thus to be delivering carbonate-rich sediment to these subduction zones. Based on the above, we consider it very likely that

“unmeasured” volcanoes in the Papua New Guinea–Northern Solomon–Vanuatu arcs belong to Group 2. We use therefore the  $\text{CO}_2/\text{S}_\text{T}$  ratio vs. Ba/La global association for Group 2 volcanoes (see Fig. 3a) to predict (based on trace element information)  $\text{CO}_2/\text{S}_\text{T}$  ratios ranging from  $2.1 \pm 0.7$  to  $2.7 \pm 0.7$  for these volcanoes (Tables 1 and S1e). We note that the two “measured” volcanoes in the central and southern Vanuatu arc (Bembow on Ambrym Island, and Yasur on Tanna Island) both exhibit Group 1 gas affinity ( $\text{CO}_2/\text{S}_\text{T}$  of 1.5–1.6), implying that the predicted C-richer gas signature for northern Vanuatu volcanoes requires validation from measurements.

## Discussion

**Validity of whole rock trace element proxy for  $\text{CO}_2/\text{S}_\text{T}$ .** Our predicted  $\text{CO}_2/\text{S}_\text{T}$  ratios stand on the assumption that gas compositions are linked to trace element compositions of their source magmas at either regional (Fig. 2) or global (Fig. 3) scale. Implicit in establishing such relationships is that gas ( $\text{CO}_2/\text{S}_\text{T}$ ) and trace-element (Ba/La) whole-rock tracers are inherited by the same processes at their source, and are similarly conserved during magma ascent, decompression and degassing/eruption<sup>36</sup>. For Ba/La, a link has been made between signatures of arc rocks and subducted sediments at corresponding tranches<sup>80</sup>, so that this and other trace element ratios are commonly used as slab-fluid proxies for characterizing the mantle source of magmas<sup>81,82</sup>. Both elements exhibit incompatible behaviour during magma differentiation, so that the source-inherited ratios are essentially conserved during magma evolution, at least for the mafic to intermediate (andesitic) magma compositions considered here (as outlined in the Method).

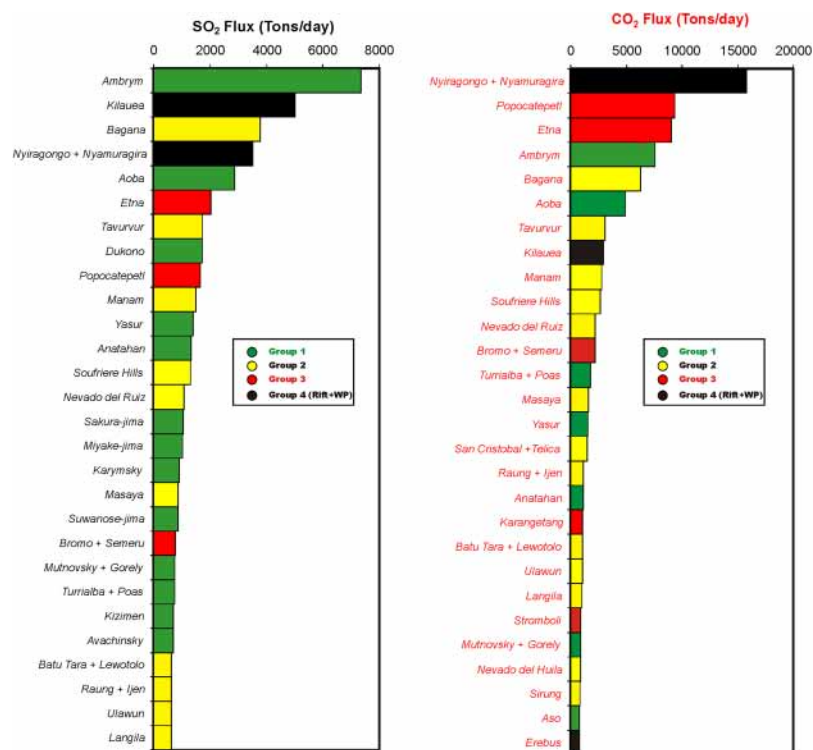
The behaviour of volatile components  $\text{CO}_2$  and S is obviously complex during the generation and evolution of slab fluids and mantle-derived magmas<sup>83</sup>. Not only are slab sources and processes only partially understood for C and S<sup>12,39</sup>, but these volatile species will be selectively extracted from melt and partitioned into the vapour phase according to their melt solubilities (that dependent in a complex fashion on magma T–P–X–redox conditions), upon magma decompression and differentiation<sup>84,85</sup>. One may thus argue that degassing-related fractionations, for which abundant model<sup>86–88</sup>, experimental<sup>89</sup> and observational<sup>90</sup> evidence exists, act as to render the  $\text{CO}_2/\text{S}_\text{T}$  ratios in both degassed melt (preserved in melt inclusions in phenocrysts) and exsolved vapour (discharged as volcanic gases) unrepresentative of the mantle source compositions, and thus unlinked<sup>91</sup> to Ba/La or other trace element proxies.

Where sufficient data exists (e.g., Figs 2a,d and 3a), however, the  $\text{CO}_2/\text{S}_\text{T}$  vs. Ba/La correlations appear systematic and statistically significant, and we consider unlikely that these associations are purely accidental. Our regional/global associations here, thus, implicate that the time-averaged  $\text{CO}_2/\text{S}_\text{T}$  ratios of volcanic gases ultimately reflect the volatile ratios in the parental (un-degassed) melt, and in the mantle source. To reconcile this with the well-established degassing-driven  $\text{CO}_2$  vs.  $\text{S}_\text{T}$  fractionations, we observe that, at least at mafic systems, comparison between measured and modelled (from numerical simulation of magma degassing paths using volatile saturation codes<sup>86–88</sup>) gas  $\text{CO}_2/\text{S}_\text{T}$  ratios typically imply equilibrium pressures (e.g., pressures of final gas–melt segregation) of 0.1–5 MPa during quiescent degassing activity<sup>29,36,84,85,92</sup>. Thus, at least during non-eruptive periods, during which the majority of the volcanic gas observations in the literature are taken, observations and models both indicate very shallow (a few hundred meters below the magma–air interface) gas segregation from the convecting feeding magmas<sup>93,94</sup>. If shallow closed-system degassing conditions<sup>85,94</sup> prevail, then the magmatic gas phase released as volcanic gas during open-vent activity does represent an integral of volatiles exsolved from melt during most ( $P > 5$  MPa) of the magma decompression path. This released magmatic gas is thus very similar in composition to the source and parental melt volatile signature, irrespective of its hydrous (for arc volcanoes) or more  $\text{H}_2\text{O}$ -poor (for non-arc systems) nature<sup>20,93</sup>. The short-lived (days to weeks) pulses of  $\text{CO}_2$ -rich gas, seen prior to eruption of mafic arc volcanoes<sup>27–29,84,92</sup>, imply somewhat deeper (typically, ~10–30 MPa) last gas–melt equilibration, but yet suggest closed-system is maintained up to rather shallow levels in a magmatic plumbing system, at least during quiescence. During basaltic explosive activity, deeper gas segregation is implied by gas observations<sup>95,96</sup>, but such eruptive degassing contributes only a minor fraction of the total degassing budget, which is dominated by passive emissions<sup>93</sup>.

The lack of a systematic correlation between volcanic gas  $\text{CO}_2/\text{S}_\text{T}$  ratios and  $\text{SO}_2$  fluxes (Fig. 5) further supports the idea that the former are not significantly affected by variable extents of magma degassing and gas–melt separation depths at various volcanoes. In mafic systems, the  $\text{SO}_2$  flux is a proxy for the rates of magma degassing in a volcano’s shallow (<3 km) plumbing system<sup>93</sup>. As such, at least in principle, shallow magma ascent and decompression should be tracked by increasing  $\text{SO}_2$  flux and decreasing  $\text{CO}_2/\text{S}_\text{T}$  ratios in the surface gas output<sup>26</sup>, a relationship that is not observed in our global dataset (Fig. 5). The  $\text{SO}_2$  flux-independent, distinct  $\text{CO}_2/\text{S}_\text{T}$  distributions of Group 1, 2 and 3 volcanoes (see Fig. 5) suggest, instead, that source signature, rather than degassing, ultimately controls the longer-term, time-averaged volcanic gas compositions. We caution that  $\text{CO}_2/\text{S}_\text{T}$  ratio volcanic gas compositions may become less source-related in intermediate to silicic systems, where the gas output is often buffered by gas–melt equilibration in crustal, vapour-saturated magma reservoirs<sup>97–100</sup>. It is thus possible that part of the scatter in our gas vs. trace-element associations (Figs 2 and 3) is caused by the intermediate (andesitic) systems included in our dataset. Silicic systems have intentionally been excluded from our compilation.

The good match between our predicted and measured  $\text{CO}_2/\text{SO}_2$  ratios at Pacaya volcano (Fig. 1) also support, although indirectly, the validity of our gas vs. trace element associations. In addition to Pacaya, recent airborne gas measurements<sup>54</sup> at Tungurahua and Cotopaxi volcanoes in Ecuador have found  $\text{CO}_2/\text{SO}_2$  ratios (in the 2 to 2.5 range) fully overlapping our predicted range ( $2.5 \pm 0.8$ ; Table 1). These successful tests provide confidence in the robustness of our predicted  $\text{CO}_2/\text{S}_\text{T}$  ratios. We caution that, in order to validate our methodology further and reduce the scatter in gas vs. trace element scatter plots (e.g., Fig. 3g), gas observations should be prioritized in remote, unexplored volcanoes in Papua New Guinea, Sandwich Islands, Solomon Islands, Sumatra, east Sunda–Banda, and north–Vanuatu. In some of these arc segments (e.g., Sumatra, Sunda), crustal C may be involved<sup>63,66,67</sup>, in which case our predicted  $\text{CO}_2/\text{S}_\text{T}$  ratios may underestimate the actual magmatic gas ratio (by a factor up to ~1.5–2). We also advise that, since only high-temperature ( $\text{SO}_2$ -dominated) gas data are used to





**Figure 6.** The 28 top-ranking volcanic point sources of SO<sub>2</sub> (left) and CO<sub>2</sub> (right) during 2005–2015. Data are from Table 1. SO<sub>2</sub> fluxes are 2005–2015 means from ref.<sup>30</sup>. The CO<sub>2</sub> fluxes are calculated from SO<sub>2</sub> using measured or predicted CO<sub>2</sub>/SO<sub>2</sub> ratios (see Table 1). Different volcano groups are identified by different colours. The global CO<sub>2</sub> budget is dominated by CO<sub>2</sub>-rich Group 2–3 arc volcanoes. Two rift volcanoes (Nyiragongo and Nyamuragira) and one within-plate (WP) volcano (Kilauea) appears in the top-10 list of CO<sub>2</sub> emitting volcanoes<sup>110</sup>.

establish our gas vs. trace-element associations (Figs 2 and 3), our predicted CO<sub>2</sub>/S<sub>T</sub> ratios are representative of the magmatic gas signature, irrespective of whether or not hydrothermal processes are acting to alter the actual and total gas volcano emissions. For example, the hydrothermal (H<sub>2</sub>S-rich) gas emissions from Marapi volcano in Sumatra have measured CO<sub>2</sub>/S<sub>T</sub> ratios of  $20.5 \pm 1.1$  (Table 1), well distinct from what we would predict (CO<sub>2</sub>/S<sub>T</sub> ratio of  $\sim 2.6$ ) using the whole-rock Ba/La ( $19 \pm 3$ ; Table S1c) and the Indonesian gas vs. trace-element relationship (Fig. 2g). As such, discrepancy between measured and predicted CO<sub>2</sub>/S<sub>T</sub> ratio at any other hydrothermal volcano may lead to apportioning the fraction of S lost to (or C produced by) the hydrothermal system. While we believe that hydrothermal processing should be the exception rather than the rule for the satellite-sensed volcanoes here, we ultimately anticipate our predicted CO<sub>2</sub>/S<sub>T</sub> ratios (Table 1) will require revision and upgrading as new high quality gas data become available for newly measured volcanoes.

One important aspect to consider is that our regional/global associations (Figs 2 and 3) are based on averaging trace element information for rocks erupted during decades to millennia of volcanic activity. As such, the CO<sub>2</sub>/S<sub>T</sub> ratios predicted from such associations should be viewed as long-term means over a volcano's lifespan, rather than the instantaneous measurements as obtainable by direct gas observations. These “geologic” gas CO<sub>2</sub>/S<sub>T</sub> ratios may thus serve, when combined with measured S content in mafic glass inclusions, to estimate the initial CO<sub>2</sub> content in parental, un-degassed melts, and eventually in the sub-arc mantle. Both are similarly poorly constrained<sup>101,102</sup> due to pre- and post-entrapment loss to vapour of poorly soluble CO<sub>2</sub>.

**A decadal global CO<sub>2</sub> flux budget.** Our predicted CO<sub>2</sub>/S<sub>T</sub> ratios are converted into CO<sub>2</sub> fluxes (Table 1) by assuming S<sub>T</sub> = SO<sub>2</sub> and scaling to the OMI-based mean SO<sub>2</sub> fluxes for the 2005–2015 period<sup>30</sup>. We focus on the OMI satellite dataset owing to advantages brought by its global and coincident observations, but yet observe that quantitatively similar results would be obtained using ground-based SO<sub>2</sub> flux observations instead<sup>15</sup>. The predicted CO<sub>2</sub> fluxes range from 57 tons/day (Kanlaon volcano in the Philippines) to 6200 tons/day (Bagana volcano in PNG) (Figs 4 and 6). Uncertainty in the derived CO<sub>2</sub> fluxes (see Table 1, column N) is based on propagation of the respective errors on SO<sub>2</sub> flux (column G) and predicted CO<sub>2</sub>/S<sub>T</sub> ratios (column I).

The total cumulative CO<sub>2</sub> emissions from the 34 “unmeasured” volcanoes (those with no measured gas information available) would thus be  $\sim 11.4 \pm 1.1$  Mt/yr ( $\sim 0.26 \pm 0.02 \cdot 10^{12}$  mol/yr), thus adding an additional  $\sim 34\%$  to the cumulative “measured” mean CO<sub>2</sub> emissions in 2005–2015 ( $27.4 \pm 3.6$  Mt/yr; Table 1). Finally, our extrapolated (measured + predicted) CO<sub>2</sub> flux budget is  $38.7 \pm 2.9$  Mt/yr (or  $0.88 \pm 0.06 \cdot 10^{12}$  mol/yr). It is important to notice that our approach, in which the CO<sub>2</sub>/S<sub>T</sub> ratio signature of each volcano is independently evaluated, leads to far better constrained CO<sub>2</sub> budget (7% uncertainty at 1 SD) that would be possible using any “averaged” volcanic

$\text{CO}_2/\text{S}_\text{T}$  ratio proxy (as has been often attempted in past studies). For example, scaling the mean global  $\text{SO}_2$  flux ( $23 \pm 15$  Mt/yr) to the mean volcanic  $\text{CO}_2/\text{S}_\text{T}$  ratio ( $2.7 \pm 3.6$ ) (all data from Table 1) would lead to a global  $\text{CO}_2$  flux of  $62 \pm 92$  Mt/yr (e.g., 148% uncertainty at 1 SD).

Based on our results, we infer that 6 strongly degassing volcanoes with time-averaged (2005–2015 means)  $\text{CO}_2$  fluxes of  $\geq 5000$  tons/day dominate the global  $\text{CO}_2$  budget (Figs 4 and 6). One of these (Bagana, PNG) is an “unmeasured” volcano and would not have been identified as a top  $\text{CO}_2$  emitter without the proxy approach developed here. It is interesting to observe that while the  $\text{SO}_2$  global budget is dominated by the Group 1 volcanoes (accounting for 13 out of the 28 strongest volcanic  $\text{SO}_2$  sources; Fig. 6), the  $\text{CO}_2$  global budget is predominantly determined by the  $\text{CO}_2$ -enriched arc volcanoes in Group 2 (13 out of 28) and Group 3 (5 out of 28, with 2 – Popocatepetl and Etna – in the top-5 list) (Fig. 6). Two continental rift volcanoes (Nyiragongo and Nyamuragira) and two within-plate volcanoes (Kilauea and Erebus) also appear in our top-28 list of volcanic  $\text{CO}_2$  emitters (Fig. 6).

Our extrapolated global  $\text{CO}_2$  flux of  $38.7 \pm 2.9$  Mt/yr is lower than previous global volcanic  $\text{CO}_2$  flux estimates in the literature, ranging from 66 to 540 Mt/yr (see ref.<sup>11</sup> for a review). Several causes can explain this mismatch.

First, and most importantly, our global volcanic  $\text{CO}_2$  budget here only includes the contribution from the “strongly degassing volcanoes” that emit  $\text{SO}_2$  in quantities large enough to be detected from space (by OMI in this specific case<sup>30</sup>). We therefore admittedly do not take into consideration in our estimate the  $\text{CO}_2$  contribution from mildly degassing “magmatic” volcanoes (those still emitting  $\text{SO}_2$ , but at levels too low to be resolved by satellites) and from “hydrothermal” volcanoes in which  $\text{CO}_2$  is emitted in combination with  $\text{H}_2\text{S}$  (instead of  $\text{SO}_2$ ). Although typically exhibiting weaker surface gas manifestations, compared to the OMI-detected volcanoes characterised here, these magmatic-hydrothermal systems do often exhibit C-rich gas compositions<sup>36</sup> (reflecting the extent/mechanism of gas-water-rock reaction with meteoric-hydrothermal fluids<sup>45</sup>), and do emit  $\text{CO}_2$  at the  $\sim 1000$  tons/day level in the most extreme cases<sup>17</sup>, but most typically in the hundreds of tons/day range<sup>15</sup>. Considering that several hundreds of volcanoes worldwide are currently undergoing mild magmatic-hydrothermal degassing activity, this emission type could be responsible for the emission of several tens of Mt  $\text{CO}_2$ /yr globally<sup>11,15</sup>. Also, we do not account for the  $\text{CO}_2$  output from volcanic lakes<sup>103</sup>, and diffuse/regional soil  $\text{CO}_2$  emissions around volcanic systems<sup>104</sup>, for which more data and alternative extrapolation approaches would be required. We therefore stress our results are not intended to represent total  $\text{CO}_2$  emissions from global subaerial volcanism, but rather the magmatic  $\text{CO}_2$  budget fraction contributed by the most actively degassing volcanoes on Earth.

Secondly, the mismatch in the estimated  $\text{CO}_2$  fluxes (this work and previous studies) derives (at least partially) from the distinct gas datasets used. We here specifically base our  $\text{CO}_2$  budget calculations on a consistent set of coincident (satellite-based)  $\text{SO}_2$  flux measurement, taken during a relatively short (decadal) period and with same retrieval/processing technique. In contrast, previous estimates have been hampered by the combination of sparse observations, taken over several decades, and with diverse observational/retrieval techniques. Even volcanoes which are persistently active alternate periods of elevated degassing with phases of reduced activity, and so non-coincident observations (taken over periods spanning several decades) may lead to biases. For example, by combining measurements taken between 1954 and 2011, a cumulative  $\text{CO}_2$  flux of 59.7 Mt/yr (from 33 measured volcanic gas plumes) was obtained<sup>11</sup>, or 2 times more than our mean 2005–2015 flux. We also explicitly use  $\text{CO}_2/\text{SO}_2$  information for high-temperature magmatic gases only, in contrast with previous efforts<sup>23</sup> in which individual arc  $\text{CO}_2$  emissions have been quantified also considering low-temperature hydrothermal gas samples in which the C-rich composition is not representative of the strongly degassing “magmatic” arc systems. We also cannot rule out that part of the discrepancy is due to our Ba/La approach, which may only represent the sub-Moho magmatic  $\text{CO}_2$  flux, and not a potentially large<sup>44</sup> recycled crustal  $\text{CO}_2$  flux. Finally, our “measured”  $\text{CO}_2$  dataset is extrapolated to the total number of “unmeasured” strongly degassing volcanoes by predicting, for each of them, the specific  $\text{CO}_2/\text{SO}_2$  ratio gas signature, rather than relying on the assumption that the global  $\text{CO}_2$  flux population obeys a specific statistical distribution (e.g., the power law distribution<sup>105</sup>).

Our results implicate that the arc volcano C flux ( $\sim 8 \pm 0.6$  Mt C/yr) corresponds to a significant amount ( $\sim 50\%$ ) of the subducted sedimentary carbonate ( $15 \pm 2$  Mt/yr; ref.<sup>106</sup>), but only a relatively small fraction ( $< 21\%$ ) of the total C input at arc trenches ( $40\text{--}114$  Mt C/yr; refs<sup>1,12</sup>). Thus, either the C input is balanced by “diffuse” C output forms, such as regional aquifers or soil degassing<sup>107</sup> in the arc crust, or a substantial fraction of the subducted C is ultimately not erupted, but rather stored either in the lithospheric mantle<sup>8</sup> or in the deep mantle<sup>1,2</sup>.

## Methods

The  $\text{SO}_2$  flux compilation<sup>30</sup> we rely on in this study includes a list of the 91 top-ranking volcanic  $\text{SO}_2$  degassing sources in 2005–2015 (Table 1). This set of consistent (identical retrieval/processing technique) and simultaneous (global) measurements has improved upon the shortcomings of previous catalogues<sup>108</sup>, which combined  $\text{SO}_2$  fluxes obtained with diverse techniques and in disparate temporal intervals (often differing by several decades).

These  $\text{SO}_2$  flux data are converted into  $\text{CO}_2$  fluxes by using either measured or predicted molar  $\text{CO}_2/\text{S}_\text{T}$  ratios. For these strongly degassing volcanoes,  $\text{S}_\text{T}$  is assumed to correspond to  $\text{SO}_2$  throughout, since  $\text{SO}_2$  detection by satellites implies limited or no interaction with hydrothermal system (and thus trivial reduced S species, such as  $\text{H}_2\text{S}$ ).

**Measured volcanoes.** For 57 out of these 91 volcanic  $\text{SO}_2$  sources, we convert  $\text{SO}_2$  fluxes into  $\text{CO}_2$  fluxes, by pairing the former with the characteristic (mean) molar  $\text{CO}_2/\text{S}_\text{T}$  ( $\text{CO}_2/\text{SO}_2$ ) ratios in the corresponding volcanic gases (Table 1). For arc volcanoes, we use the time-averaged molar  $\text{CO}_2/\text{SO}_2$  ratios compiled by (ref.<sup>36</sup>), integrated with novel gas information for eight new targets that have only recently been measured for the first time (see Table 1 for data provenance). Arc volcanoes are ranked in Groups (1 to 3) following the original categorization<sup>36</sup>. For non-arc volcanoes (here referred as Group 4), we average available volcanic gas information in the literature (see Table 1 for data sources). Note that, for both arc and non-arc, in cases where more than one volcano are listed



in the original dataset<sup>30</sup> (e.g., Nyiragongo + Nyamuragira) due to insufficient spatial OMI resolution, we averaged the available volcanic gas information for the individual volcanoes, weighting each volcano's  $\text{CO}_2/\text{S}_\text{T}$  ratio by its ground-based S flux (where available) to obtain a combined  $\text{CO}_2/\text{S}_\text{T}$  ratio for the pair (see Table 1).

**Unmeasured volcanoes.** Thirty-four out of the 91 top-ranking volcanic  $\text{SO}_2$  sources<sup>30</sup> have never been characterised for volcanic gas composition (Table 1). These include four of the top-ten ranking volcanic  $\text{SO}_2$  emitters<sup>30</sup> (Bagana, Rabaul and Manam in Papua New Guinea, and Aoba in the Vanuatu archipelagos; Fig. 4). To indirectly infer the molar  $\text{CO}_2/\text{S}_\text{T}$  ratio gas signature of each of these 34 volcanoes, we use the averaged (mean) trace-element composition of the corresponding volcanic rocks. To this aim, as in earlier work<sup>36</sup>, we extract trace-element information (Ba, La, Sr, Nd, U and Th whole-rock concentrations) either from the Earthchem data-portal (<http://www.earthchem.org/>), or from other sources (for volcanoes that do not appear on Earthchem) (see Table S1). Mafic to intermediate (<55%  $\text{SiO}_2$ ) rocks are only considered, same as in other work<sup>409</sup>. From these, we calculate, for each volcano, the mean ( $\pm 1$  SD) of the Ba/La whole-rock ratios (Sr/Nd and U/Th ratios were also calculated; see Table S1). These ratios, in combination with the gas vs. whole-rock relationships illustrated in Figs 1–3, are finally used, to predict the characteristic volcanic gas  $\text{CO}_2/\text{S}_\text{T}$  ratio signature for each of the 34 “unmeasured” volcanoes.

The procedure is exemplified in Fig. 1 for the Pacaya volcano example. We select Pacaya because the recently obtained gas compositions<sup>46</sup> can serve as a test of the methodology. The initial step involves establishing the relationship between  $\text{CO}_2/\text{S}_\text{T}$  gas ratios and whole-rock Ba/La ratios, using data for volcanoes for which both gas and trace element data are available (see Fig. 1; Table S1). The  $\text{CO}_2/\text{SO}_2$  vs. Ba/La relationship can be established at the scale of individual arc segments (e.g., Figs 1 and 2), or for volcano Groups<sup>36</sup> (Groups 1 or 2) (Fig. 3). For the Pacaya example, we rely on gas/whole-rock information for the well-characterised Central American Volcanic Arc (CAVA; Fig. 1). Secondly, we use regression analysis to fit the gas vs. trace-element association via either a (i) linear or (ii) logarithm regression model (Fig. 1). We find that linear regression yields the best data fit in the majority of the cases (see the Pacaya example, Fig. 1a,b), and this regression model is used throughout unless where indicated (see Table S1). We also find that data fitting is systemically optimised when the DMM composition is included in the fitting procedure (compare Fig. 1a,b), and this option is maintained throughout. Note, however, the method output (e.g., the outputted  $\text{CO}_2/\text{S}_\text{T}$  ratio) is poorly sensitive to this choice (see Table 2). Finally, the adopted regression model function (RM3 in the Pacaya example; Fig. 1 and Table 2) is used to calculate a “predicted” gas  $\text{CO}_2/\text{S}_\text{T}$  from available Ba/La information (Fig. 1). The confidence interval or delta, calculated from the regression line and one standard deviation about the regression, is taken as a proxy for the uncertainty in the predicted  $\text{CO}_2/\text{S}_\text{T}$  ratios. Uncertainty on the predicted ratios, as derived, incorporates (although indirectly) uncertainty/variability in “measured” gas  $\text{CO}_2/\text{S}_\text{T}$  ratios (average uncertainty at  $1\sigma$ , ~26%) and whole-rock Ba/La ratios (average uncertainty at  $1\sigma$ , ~16%) (see Table S1). In the specific Pacaya example (Fig. 1 and Table 2), our “predicted” gas  $\text{CO}_2/\text{SO}_2$  ratio ( $1.4 \pm 0.75$ ) matches well the recently measured<sup>45</sup> magmatic gas range ( $\text{CO}_2/\text{SO}_2$  ratio of  $1.1 \pm 1.0$ ). Our tests show that remarkably similar  $\text{CO}_2/\text{SO}_2$  ratios (see Table 2) are obtained using other trace-element slab fluid tracers, such as the Sr/Nd ratio (Fig. 1c). We opt in the following for the Ba/La regression model because (i) La is more frequently available than Nd in the Earthchem dataset for the majority of the volcanoes, and (ii) use of the Sr/Nd ratio requires a priori knowledge of volcano affinity for a specific Group (Group 1 and 2 typically exhibit diverse distributions in a  $\text{CO}_2/\text{SO}_2$  vs. Sr/Nd scatter plot; see Fig. 1c). This latter information is frequently not a priori available (see below). The same procedure is applied to all unmeasured volcanoes (Table S1a), and the “predicted” ratios (assumed to correspond to  $\text{CO}_2/\text{SO}_2$ ) are combined with  $\text{SO}_2$  flux results to ultimately infer the  $\text{CO}_2$  fluxes (Table 1).

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## Author Contributions

A.A. conceived the idea. All of the authors participated in data collection and interpretation. A.A. drafted the manuscript with the help of all co-authors.

## Additional Information

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