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tribution of split 520 observations, which in many instances occur beneath continental regions, such as North America and Eastern Asia (*I–4*), under which extensive subduction has taken place. Splitting beneath the Indian Ocean and Africa, on the other hand, may be caused by the presence of particularly fertile mantle.

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- At equilibrium the standard state free energy change  $\Delta G_{p,T}^0$  for the reaction in Eq. 1 is related to the activities of the reacting components by the equation  $\Delta G_{p,T}^0 = -RT \ln K = -RT \ln \left[ \frac{a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}}}{a_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}} \left[ a_{\text{Mg}_2\text{Si}_4\text{O}_{12}}^{\text{Gt}} \right]^3} \right]$ , where  $R$  is the gas constant,  $K$  is the equilibrium constant, and the superscript Gt refers to garnet. The component activities are described by  $a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}} = \gamma_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}} (X_{\text{Maj}}^{\text{Gt}})^3$ ,  $a_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}} = \gamma_{\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Gt}} (1 - X_{\text{Maj}}^{\text{Gt}}) (X_{\text{Ca}}^{\text{dodec}})^3$  and  $a_{\text{Mg}_2\text{Si}_4\text{O}_{12}}^{\text{Gt}} = \gamma_{\text{Mg}_2\text{Si}_4\text{O}_{12}}^{\text{Gt}} (1 - X_{\text{Maj}}^{\text{Gt}}) (X_{\text{Mg}}^{\text{dodec}})^3$ , where  $\gamma$  is an activity coefficient,  $x$  is the component mole fraction, and oct and dodec refer to the octohedral and dodecahedral cation sites of garnet and majorite (Maj). After calculating activity coefficients for mixing on just the dodecahedral site with use of a symmetric ternary solution model (for Mg, Ca, and Fe), we fit calculated values for the  $RT \ln K$  term to obtain the equation  $\Delta G_{p,T}^0 = 140763 + 26.7737P - 12560P$ . The ternary solution model uses the Margules interaction parameters  $W_{\text{FeMg}} = 300$  (J/mol) and  $W_{\text{CaFe}} = 2000$  (J/mol) taken from the literature (17), whereas the parameter  $W_{\text{MgCa}} = 8000 + 300P$  (J/mol,  $P$  in GPa) is refined by using the experimental data (13). Trial refinements showed no improvement to the fit of the data when nonideal mixing on the garnet octahedral site was included or when a reciprocal solution model was used.
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## The Chlorine Isotope Composition of Earth's Mantle

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Chlorine stable isotope compositions ( $\delta^{37}\text{Cl}$ ) of 22 mid-ocean ridge basalts (MORBs) correlate with Cl content. The high- $\delta^{37}\text{Cl}$ , Cl-rich basalts are highly contaminated by Cl-rich materials (seawater, brines, or altered rocks). The low- $\delta^{37}\text{Cl}$ , Cl-poor basalts approach the composition of uncontaminated, mantle-derived magmas. Thus, most or all oceanic lavas are contaminated to some extent during their emplacement. MORB-source mantle has  $\delta^{37}\text{Cl} \leq -1.6$  per mil (‰), which is significantly lower than that of surface reservoirs ( $\sim 0$ ‰). This isotopic difference between the surface and deep Earth results from net Cl isotopic fractionation (associated with removal of Cl from the mantle and its return by subduction over Earth history) and/or the addition (to external reservoirs) of a late volatile supply that is  $^{37}\text{Cl}$ -enriched.

Chloride is the major anion in most geological fluids. Chlorine is volatile, incompatible during silicate melting, and water soluble. For these reasons, geological processes—including partial melting, magma degassing, hydrothermal activity, and weathering—have concentrated Cl at the surface, particularly in the ocean, evaporites, and crustal brines. Considering only the MORB-source mantle and surface reservoirs, we can estimate that the former, with 1 to 8 parts per million (ppm) of Cl (*I–3*), contributes a maximum of  $\sim 20\%$  to the Cl budget and perhaps much less, given the difficulty in obtaining a complete inventory of crustal brines. Earth's Cl budget may thus differ from that of most other abundant and geochemically important volatiles (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ).

There are several first-order questions about Cl in Earth: What early solar system processes determined Earth's initial Cl budget? How, and when, was most of Earth's Cl extracted from the mantle? How much Cl is returned to the mantle by subduction? Is the extraction of Cl from, and its return to, the mantle in steady state? If not, what can we learn about the history of Earth's volatile cycles by reconstructing secular changes in the Cl budgets of the mantle and/or surface? These questions can be addressed by determining  $\delta^{37}\text{Cl}$  (4) of the various reservoirs in that budget and isotopic fractionations associated with exchanges between those reservoirs. Surface reservoirs (mostly oceans, brines, and evaporites) are known to have a collective mean  $\delta^{37}\text{Cl}$  of  $0.0 \pm 0.5$ ‰ (5–8). However, it is more difficult to

measure the  $\delta^{37}\text{Cl}$  of pristine mantle rocks and mantle-derived magmas because both are generally poor in Cl (*I–3*), which is usually present in insoluble form. Here, we present measurements of 22 MORBs that define the mantle composition to lower  $\delta^{37}\text{Cl}$  values than previously assumed (9, 10) and use these results to examine the origin and history of Earth's volatiles.

The first attempt to define the Cl isotope composition of the mantle used thermal ionization mass spectrometry (TIMS) to analyze three MORB samples (9), yielding an average mantle value of  $+4.7$ ‰. Sharp *et al.* (10) recently used gas-source mass spectrometry to determine a mantle  $\delta^{37}\text{Cl}$  value of  $-0.1 \pm 0.4$ ‰, which was derived from the average of 11 MORB samples, two kimberlites, and three carbonatites. They suggested  $\delta^{37}\text{Cl}$  homogeneity near the seawater value (0‰) for mantle and surface reservoirs over Earth's history (10). This implies that neither removal of Cl from the mantle nor its

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return by subduction led to substantial net Cl isotopic fractionation (isotopic steady state). Such a conclusion is consistent with the apparent (i) lack of secular change in  $\delta^{37}\text{Cl}$  in sediments (10) [although data include large, unexplained variations about the long-term mean, from  $-3.2$  to  $+2.5\%$  (10)] and (ii) lack of Cl isotope fractionation through the subduction-related partial loss of Cl (11) inherited from oceanic alteration. However, Cl isotope fractionation of up to  $8\%$  has been seen in surface reservoirs during alteration of the oceanic lithosphere (11–15) and/or in sedimentary settings (16–18).

We determined the Cl contents and isotopic compositions of 22 MORB samples using a low-blank method (15, 19) involving the extraction of structurally bound Cl by pyrohydrolysis, followed by gas-source, dual-inlet mass spectrometric measurements. Analytical yields average  $100 \pm 8\%$ , blanks are typically 7% of the sample chloride analyzed, and the whole-procedure external precision for  $\delta^{37}\text{Cl}$  measurements ( $1\sigma$ ) is  $\pm 0.14\%$  (fig. S1). Our samples are nominally zero-age lavas collected from the Pacific, Atlantic, and Indian oceans and cover large ranges in extent of fractional crystallization [MgO, 5.9 to 9.2 weight percent (wt %)], partial melting [ $\text{Na}_2\text{O}$  corrected for crystal fractionation to  $8\%$  MgO ( $\text{Na}_{8,0}$ ), 1.9 to 4.2 wt %], source enrichment (K/Ti, 0.04 to 0.41), eruption depths [1800 to 4905 meters below sea level (mbsl)], spreading rate (16 to  $153 \text{ mm yr}^{-1}$ ), and degree of Cl contamination (K/Cl, 1.0 to 38.3) (table S1). There is substantial evidence that some terrestrial lavas are contaminated with surficial Cl to some extent (1, 2, 20, 21) because of the enormous contrast in Cl concentrations between primary magmas (about  $<80$  ppm) and surficial waters and rocks (typically 1000s ppm). Our sample suite spans a relatively large range in Cl concentration (42 to 701 ppm), so we can examine how the samples vary with isotopic composition.

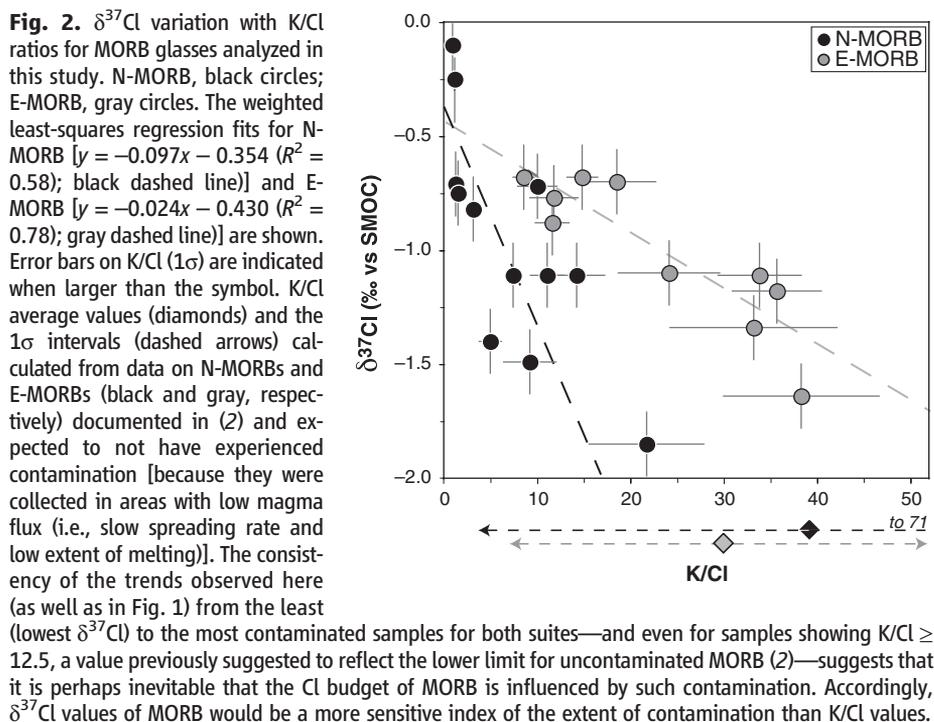
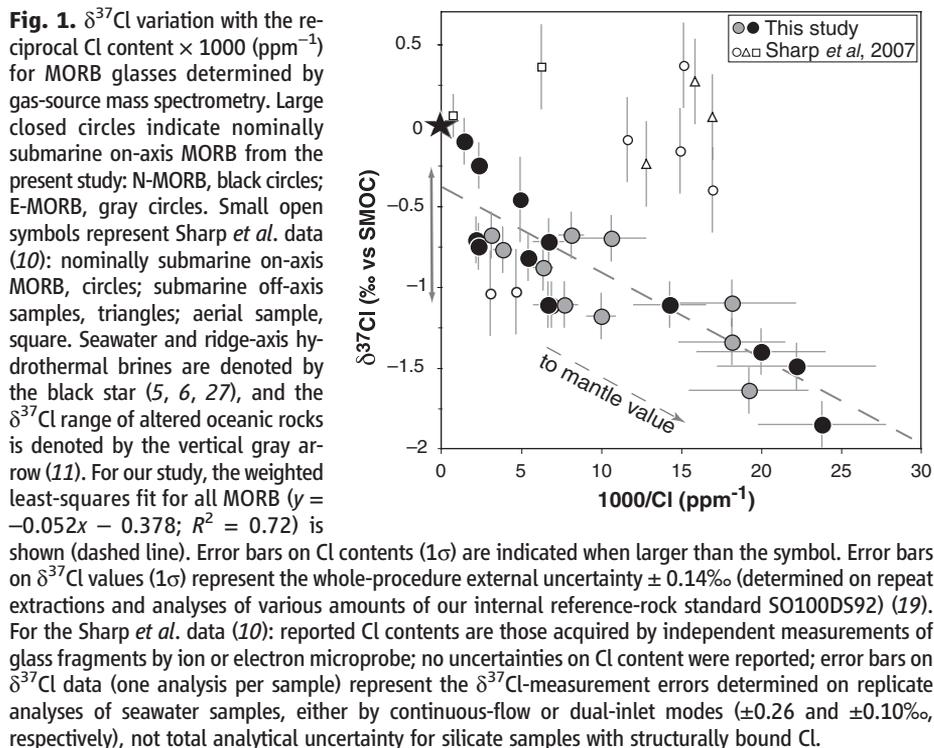
Our  $\delta^{37}\text{Cl}$  values for MORB glasses range from  $-1.9$  to  $-0.1\%$  and increase with Cl concentration (Fig. 1). The most Cl-rich samples have  $\delta^{37}\text{Cl}$  values close to seawater [ $\delta^{37}\text{Cl} = 0\%$  (5, 6)], whereas Cl-poor MORBs have substantially lower  $\delta^{37}\text{Cl}$  values.

One hypothetical explanation of the linear  $\delta^{37}\text{Cl}$  versus  $1/\text{Cl}$  ( $\delta^{37}\text{Cl}$ -1/Cl) trend is that all MORBs have  $\delta^{37}\text{Cl}$  values near  $0\%$ , and our analytical technique contributed a low- $\delta^{37}\text{Cl}$  blank that decreased the measured values of Cl-poor samples. Our analytical blank has a  $\delta^{37}\text{Cl}$  value of  $-0.3 \pm 2.2\%$  (fig. S2), which is far above the value of  $-9.8 \pm 4.3\%$  needed to explain the trend in Fig. 1. Thus, the  $\delta^{37}\text{Cl}$ -1/Cl trend reflects real, coupled variations in Cl concentration and isotopic composition of MORBs, not laboratory contamination. Because Cl is highly incompatible [partition coefficient  $D_{\text{herzolite/silicate-melt}} \sim 0.002$  (22)] and does not undergo speciation changes by partitioning between silicate minerals and melts during crystallization or melting, variable degrees of partial melting or extents

of crystallization should produce only negligible Cl isotope fractionation at magmatic temperatures (23, 24). Because our MORBs were collected from relatively great depths ( $\geq 1800$  mbsl) and have relatively low Cl contents ( $\leq 701$  ppm), they remained undersaturated with Cl during eruption (25, 26) and should not have lost Cl by degassing. Thus, the  $\delta^{37}\text{Cl}$ -1/Cl trend reflects

mixing between two (or more) isotopically distinct components that are commonly sampled during the generation, differentiation, and/or eruption of MORBs.

The  $\delta^{37}\text{Cl}$ -1/Cl trend might reflect mixing between primary mantle Cl and Cl added pre- or syn-eruptively to those magmas, such as what might result from contamination (assimilation) of mag-



mas by a Cl-rich, seawater-derived material (e.g., seawater, brines, and altered rocks) (1, 2, 20, 21). According to this hypothesis, the Cl-poor, low- $\delta^{37}\text{Cl}$  end of the trend (Fig. 1) most closely approaches the composition of primary MORB, and increasing degrees of mixing with seawater-derived Cl increase their Cl contents and draw the  $\delta^{37}\text{Cl}$  values of the most contaminated lavas toward the value of seawater. Several independent lines of evidence support such an interpretation: (i) the high- $\delta^{37}\text{Cl}$  end-member of the mixing trend is within the range of compositions of seawater or on-axis high-temperature hydrothermal fluids [both  $\sim 0\text{‰}$  (5, 6, 27)] and altered oceanic rocks [about  $-0.7 \pm 0.4\text{‰}$  (11)]; (ii) the Cl contents of our lowest  $\delta^{37}\text{Cl}$  samples imply a typical mantle Cl concentration of less than  $4 \pm 3$  ppm [assuming MORBs are typically produced by 10% mantle melting and Cl is highly incompatible during mantle melting (22)], within the previously suggested range (1 to 8 ppm) (1–3); and (iii) MORBs from relatively fast-spreading ridges, expected to have experienced larger extents of contamination (1, 2, 20, 21), show higher  $\delta^{37}\text{Cl}$  values (closer to 0‰) than MORBs from relatively slow-spreading ridges (averages for Pacific and Indian samples of  $-0.8$  and  $-1.4\text{‰}$ , respectively). Because K is an incompatible element and is enriched in lavas due to assimilation far less than Cl is, K/Cl ratios have been used as an index of assimilation (1, 2, 20). Thus, the fact that our samples with the lowest K/Cl values also have the highest  $\delta^{37}\text{Cl}$  (and vice versa; samples SO22-17D and MD57D-7-2, respectively) supports our interpretations of the trend in Fig. 1 (i.e., high-Cl, high- $\delta^{37}\text{Cl}$  samples are more contaminated than those with low Cl and low  $\delta^{37}\text{Cl}$ ). It is noteworthy that, whereas normal-MORBs (N-MORBs) and enriched-MORBs (E-MORBs) define a common trend in Fig. 1, they appear to define two distinct trends in a  $\delta^{37}\text{Cl}$  versus K/Cl plot (Fig. 2): Starting at a common intercept at low K/Cl and high  $\delta^{37}\text{Cl}$ , K/Cl increases gradually with decreasing  $\delta^{37}\text{Cl}$  in N-MORB and relatively strongly in E-MORB. Among the least contaminated samples (i.e., those with the lowest  $\delta^{37}\text{Cl}$  values), E-MORBs have K/Cl ratios about twice those of N-MORBs at a given  $\delta^{37}\text{Cl}$  value. It is possible that the distinction between the N- and E-MORB trends in Fig. 2 is fortuitous and would not be observed in a broader and more representative sampling. In particular, N- and E-MORBs have been distinguished here by their K/Ti ratios, though Ti is heterogeneous in the mantle (28, 29). Also, the distinct K/Cl ratios among our E- and N-MORB samples result mainly from higher K contents of E-MORBs, not from distinct Cl contents. Nevertheless, this result, taken at face value, could reflect differences in K/Cl ratio and/or  $\delta^{37}\text{Cl}$  value between the mantle sources of E- and N-MORBs. At one extreme, the mantle sources of N- and E-MORBs may be comparable in  $\delta^{37}\text{Cl}$ , but E-MORBs are higher in K/Cl ratios than N-MORBs [contrary to what has been previously suggested; e.g., (2)]. One possible explanation for such a difference is that E-MORB sources

contain larger fractions of subducted material that are rich in K but relatively poor in Cl, perhaps because most of Cl in subducted slabs is returned to the surface by arc volcanism rather than being efficiently recycled. Alternatively, these two types of mantle sources might be similar in K/Cl ratio ( $\sim 34$ ; see diamonds in Fig. 2), but N-MORB sources are lower in  $\delta^{37}\text{Cl}$  than E-MORB sources.

Assuming that our MORB samples with the lowest Cl concentrations are the least contaminated by seawater-derived Cl, we estimate that the MORB-source mantle (depleted and enriched parts) is characterized by a  $\delta^{37}\text{Cl}$  value of  $-1.6\text{‰}$  or less, which is lower than values previously proposed (9, 10). The different value of Magenheimer *et al.* (9) can be ascribed to analytical errors in the TIMS-based measurements (15). The cause of the difference from the results of Sharp *et al.* (10)—the methods of which are more similar (though not identical) to ours—is unclear. Assuming that both data sets are analytically accurate, it is difficult to ascribe the discrepancy to a difference in sample selection, because their suite includes some samples with relatively high  $\delta^{37}\text{Cl}$  and low nominal Cl contents, which is incompatible with the  $\delta^{37}\text{Cl}$ -Cl/Cl trend for our data (Fig. 1). It also seems unlikely that the diverse suite of nominally MORBs we examined (from the three main oceans and showing large variations in parameters such as  $\text{Na}_{8,0}$ , K/Ti, K/Cl, and spreading rate) would yield the simple  $\delta^{37}\text{Cl}$ -Cl/Cl trend that we found if low-Cl, high- $\delta^{37}\text{Cl}$  MORBs were common. Given that Sharp *et al.* (10) report neither Cl contents of basalts from the actual extractions of Cl for isotopic analysis nor analytical yields, a close comparison of the two data sets is not possible.

The coherence of the observed trends suggests that the mantle  $\delta^{37}\text{Cl}$  value unmodified by contamination is  $\leq -1.6\text{‰}$ , which is significantly more negative than that of the surface reservoirs ( $\sim 0\text{‰}$ ). This isotopic difference might result from (i) systematic  $^{37}\text{Cl}$  enrichment in surface reservoirs and corresponding depletion in the mantle via long-term Cl extraction from and return to the mantle and/or (ii) a primary  $^{37}\text{Cl}$  enrichment of the surface Cl of early Earth due to a late supply of volatile-rich material (30), which was enriched with  $^{37}\text{Cl}$  as compared with the material from which Earth was mainly accreted. In the first case, because the mantle now contains at least one-fifth as much Cl as surface reservoirs, any  $\delta^{37}\text{Cl}$  variations resulting from these long-term exchanges will be more important in the mantle or mantle-derived magmas than in the oceans or sedimentary rocks. The second hypothesis finds support from our current knowledge of the Cl cycle, because the subduction flux shows substantially higher  $\delta^{37}\text{Cl}$  (preliminarily estimated from serpentinites, average  $\delta^{37}\text{Cl} = -0.7 \pm 0.4\text{‰}$ ) (11) than the mantle flux ( $\delta^{37}\text{Cl} \leq -1.6\text{‰}$ ); such a combination of fluxes could only have decreased the  $\delta^{37}\text{Cl}$  gap between mantle and surface reservoirs over the long-term exchanges.

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## Supporting Online Material

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