tribution of split 520 observations, which in many instances occur beneath continental regions, such as North America and Eastern Asia (*1–4*), 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.

References and Notes

1. A. Deuss, J. Woodhouse, *Science* **294**, 354 (2001).
2. H. J. Gilbert, A. F. Sheehan, K. G. Dueker, P. Molnar, *J. Geophys. Res.* **108**, 10.1029/2001JB001194 (2003).
3. A. Deuss, S. A. T. Redfern, K. Chambers, J. H. Woodhouse, *Science* **311**, 198 (2006).
4. M. van der Meijde, S. Van der Lee, D. Giardini, *Phys. Earth Planet. Inter.* **148**, 233 (2005).
5. P. M. Shearer, *Nature* **344**, 121 (1990).
6. J. J. Ita, L. Stixrude, *J. Geophys. Res.* **97**, 6849 (1992).
7. T. Gasparik, *Contrib. Mineral. Petrol.* **124**, 139 (1996).
8. K. Hirose, Y. Fei, *Geochim. Cosmochim. Acta* **66**, 2099 (2002).
9. K. D. Litasov, E. Ohtani, *Phys. Earth Planet. Inter.* **150**, 239 (2005).
10. Y. Nishihara, E. Takahashi, *Earth Planet. Sci. Lett.* **190**, 65 (2001).
11. G. R. Helffrich, B. J. Wood, *Nature* **412**, 501 (2001).
12. D. J. Weidner, Y. Wang, in *Earth's Deep Interior: Mineral Physics and Tomography From the Atomic to the Global Scale* [*Geophys. Monogr. 117 Am. Geophys. Union* (2000)], pp. 215–235.
13. Materials and methods are available on *Science* Online.
14. D. J. Frost, *Earth Planet. Sci. Lett.* **216**, 313 (2003).
15. K. Matsuzaka, M. Akaogi, T. Suzuki, T. Suda, *Phys. Chem. Miner.* **27**, 310 (2000).
16. At equilibrium the standard state free energy change $\Delta G^0_{P,T}$ for the reaction in Eq. 1 is related to the activities of the reacting components by the equation $\Delta G^0_{P,T} =$
$$-RT\ln K = -RT\ln\left[a^{\mathrm{Gt}}_{\mathrm{Mg_3Al_2Si_3O_{12}}}\right]\Big/\left[a^{\mathrm{Gt}}_{\mathrm{Ca_3Al_2Si_3O_{12}}}\right]\left[a^{\mathrm{Gt}}_{\mathrm{Mg_4Si_4O_{12}}}\right]^{\frac{3}{4}},$$
where R is the gas constant, K is the equilibrium constant, and the superscript Gt refers to garnet. The component activities are described by
$$a^{\mathrm{Gt}}_{\mathrm{Mg_4Si_4O_{12}}} = \gamma^{\mathrm{Gt}}_{\mathrm{Mg_4Si_4O_{12}}}(X^{\mathrm{oct}}_{\mathrm{Maj}})(X^{\mathrm{dodec}}_{\mathrm{Mg}})^3,$$
$$a^{\mathrm{Gt}}_{\mathrm{Ca_3Al_2Si_3O_{12}}} = \gamma^{\mathrm{Gt}}_{\mathrm{Ca_3Al_2Si_3O_{12}}}\left(1 - X^{\mathrm{oct}}_{\mathrm{Maj}}\right)\left(X^{\mathrm{dodec}}_{\mathrm{Ca}}\right)^3 \text{ and}$$
$$a^{\mathrm{Gt}}_{\mathrm{Mg_3Al_2Si_3O_{12}}} = \gamma^{\mathrm{Gt}}_{\mathrm{Mg_3Al_2Si_3O_{12}}}\left(1 - X^{\mathrm{oct}}_{\mathrm{Maj}}\right)\left(X^{\mathrm{dodec}}_{\mathrm{Mg}}\right)^3, \text{ where}$$
γ 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 $\Delta G^0_{P,T} = 140763 + 26.773T - 12560P$. The ternary solution model uses the Margules interaction parameters $W_{\mathrm{FeMg}} = 300$ (J/mol) and $W_{\mathrm{CaFe}} = 2000$ (J/mol) taken from the literature (*17*), whereas the parameter $W_{\mathrm{MgCa}} = 8000 + 300P$ (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.
17. H. St. C. O'Neill, B. J. Wood, *Contrib. Mineral. Petrol.* **70**, 59 (1979).
18. W. F. McDonough, S.-s. Sun, *Chem. Geol.* **120**, 223 (1995).
19. G. R. Helffrich, B. J. Wood, *Geophys. J. Int.* **126**, F7 (1996).
20. L. Stixrude, *J. Geophys. Res.* **102**, 14835 (1997).
21. L. Li *et al.*, *Phys. Earth Planet. Inter.* **155**, 249 (2006).
22. S. V. Sinogeikin, J. D. Bass, *Geophys. Res. Lett.* **28**, 4335 (2001).
23. S. V. Sinogeikin, J. D. Bass, *Geophys. Res. Lett.* **29**, 10.1029/2001GL013937 (2002).
24. A. Suzuki *et al.*, *Geophys. Res. Lett.* **27**, 803 (2000).
25. A. M. Dziewonski, D. L. Anderson, *Phys. Earth Planet. Inter.* **25**, 297 (1981).
26. P. M. Shearer, *J. Geophys. Res.* **101**, 3053 (1996).
27. M. P. Flanagan, P. M. Shearer, *J. Geophys. Res.* **103**, 2673 (1998).
28. U. R. Christensen, *J. Geophys. Res.* **102**, 22435 (1997).
29. H. Kárason, R. D. Van der Hilst, in *The History and Dynamics of Global Plate Motion* (*Geophys. Monogr. 121 Am. Geophys. Union* (2000)], pp. 277–288.
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Tables S1 to S4

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The Chlorine Isotope Composition of Earth's Mantle

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Chlorine stable isotope compositions (δ^{37}Cl) of 22 mid-ocean ridge basalts (MORBs) correlate with Cl content. The high-δ^{37}Cl, Cl-rich basalts are highly contaminated by Cl-rich materials (seawater, brines, or altered rocks). The low-δ^{37}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 δ^{37}Cl ≤ –1.6 per mil (‰), which is significantly lower than that of surface reservoirs (~ 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}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 (*1–3*), contributes a maximum of ~ 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., H_2O, 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 δ^{37}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 δ^{37}Cl of 0.0 ± 0.5‰ (*5–8*). However, it is more difficult to measure the δ^{37}Cl of pristine mantle rocks and mantle-derived magmas because both are generally poor in Cl (*1–3*), which is usually present in insoluble form. Here, we present measurements of 22 MORBs that define the mantle composition to lower δ^{37}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 δ^{37}Cl value of –0.1 ± 0.4‰, which was derived from the average of 11 MORB samples, two kimberlites, and three carbonatites. They suggested δ^{37}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 δ^{37}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 ± 8%, blanks are typically 7% of the sample chloride analyzed, and the whole-procedure external precision for δ^{37}Cl measurements (1σ) is ± 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 [Na_2O corrected for crystal fractionation to 8% MgO ($Na_{8.0}$), 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 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 δ^{37}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 δ^{37}Cl values close to seawater [δ^{37}Cl = 0‰ (*5*, *6*)], whereas Cl-poor MORBs have substantially lower δ^{37}Cl values.

One hypothetical explanation of the linear δ^{37}Cl versus 1/Cl (δ^{37}Cl-1/Cl) trend is that all MORBs have δ^{37}Cl values near 0‰, and our analytical technique contributed a low-δ^{37}Cl blank that decreased the measured values of Cl-poor samples. Our analytical blank has a δ^{37}Cl value of –0.3 ± 2.2‰ (fig. S2), which is far above the value of –9.8 ± 4.3‰ needed to explain the trend in Fig. 1. Thus, the δ^{37}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 $D_{\text{lherzolite/silicate-melt}}$ ~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 (≥ 1800 mbsl) and have relatively low Cl contents (≤701 ppm), they remained undersaturated with Cl during eruption (*25*, *26*) and should not have lost Cl by degassing. Thus, the δ^{37}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 δ^{37}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-

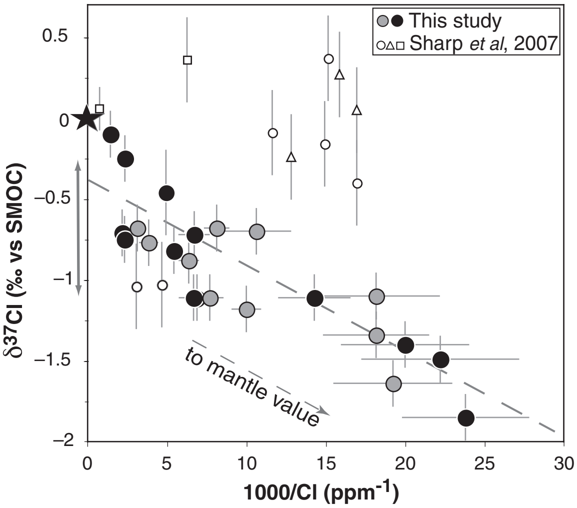

Fig. 1. δ^{37}Cl variation with the reciprocal Cl content × 1000 (ppm^{-1}) for MORB glasses determined by gas-source mass spectrometry. Large closed circles indicate nominally submarine on-axis MORB from the present study: N-MORB, black circles; E-MORB, gray circles. Small open symbols represent Sharp *et al*. data (*10*): nominally submarine on-axis MORB, circles; submarine off-axis samples, triangles; aerial sample, square. Seawater and ridge-axis hydrothermal brines are denoted by the black star (*5*, *6*, *27*), and the δ^{37}Cl range of altered oceanic rocks is denoted by the vertical gray arrow (*11*). For our study, the weighted least-squares fit for all MORB ($y = -0.052x - 0.378$; $R^2 = 0.72$) is shown (dashed line). Error bars on Cl contents (1σ) are indicated when larger than the symbol. Error bars on δ^{37}Cl values (1σ) represent the whole-procedure external uncertainty ± 0.14‰ (determined on repeat extractions and analyses of various amounts of our internal reference-rock standard SO100DS92) (*19*). For the Sharp *et al*. data (*10*): reported Cl contents are those acquired by independent measurements of glass fragments by ion or electron microprobe; no uncertainties on Cl content were reported; error bars on δ^{37}Cl data (one analysis per sample) represent the δ^{37}Cl-measurement errors determined on replicate analyses of seawater samples, either by continuous-flow or dual-inlet modes (±0.26 and ±0.10‰, respectively), not total analytical uncertainty for silicate samples with structurally bound Cl.

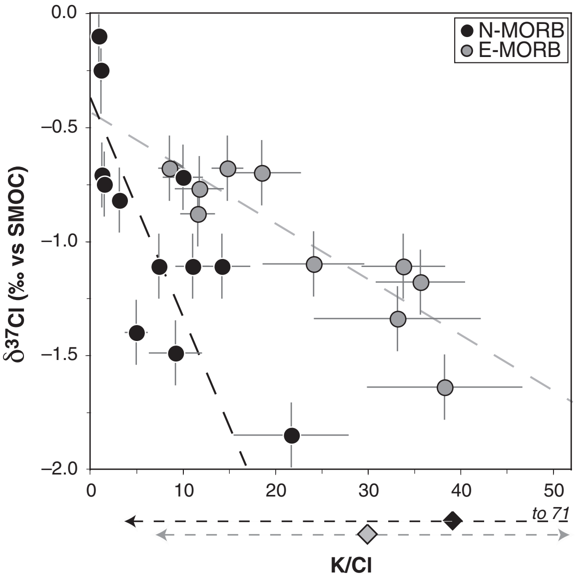

Fig. 2. δ^{37}Cl variation with K/Cl ratios for MORB glasses analyzed in this study. N-MORB, black circles; E-MORB, gray circles. The weighted least-squares regression fits for N-MORB [$y = -0.097x - 0.354$ ($R^2 = 0.58$); black dashed line)] and E-MORB [$y = -0.024x - 0.430$ ($R^2 = 0.78$); gray dashed line)] are shown. Error bars on K/Cl (1σ) are indicated when larger than the symbol. K/Cl average values (diamonds) and the 1σ intervals (dashed arrows) calculated from data on N-MORBs and E-MORBs (black and gray, respectively) documented in (*2*) and expected to not have experienced contamination [because they were collected in areas with low magma flux (i.e., slow spreading rate and low extent of melting)]. The consistency of the trends observed here (as well as in Fig. 1) from the least (lowest δ^{37}Cl) to the most contaminated samples for both suites—and even for samples showing K/Cl ≥ 12.5, a value previously suggested to reflect the lower limit for uncontaminated MORB (*2*)—suggests that it is perhaps inevitable that the Cl budget of MORB is influenced by such contamination. Accordingly, δ^{37}Cl values of MORB would be a more sensitive index of the extent of contamination than K/Cl values.

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-δ^{37}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 δ^{37}Cl values of the most contaminated lavas toward the value of seawater. Several independent lines of evidence support such an interpretation: (i) the high-δ^{37}Cl end-member of the mixing trend is within the range of compositions of seawater or on-axis high-temperature hydrothermal fluids [both ~ 0‰ (*5*, *6*, *27*)] and altered oceanic rocks [about –0.7 ± 0.4‰ (*11*)]; (ii) the Cl contents of our lowest δ^{37}Cl samples imply a typical mantle Cl concentration of less than 4 ± 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 δ^{37}Cl values (closer to 0‰) than MORBs from relatively slow-spreading ridges (averages for Pacific and Indian samples of –0.8 and –1.4‰, 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 δ^{37}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-δ^{37}Cl samples are more contaminated than those with low Cl and low δ^{37}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 δ^{37}Cl versus K/Cl plot (Fig. 2): Starting at a common intercept at low K/Cl and high δ^{37}Cl, K/Cl increases gradually with decreasing δ^{37}Cl in N-MORB and relatively strongly in E-MORB. Among the least contaminated samples (i.e., those with the lowest δ^{37}Cl values), E-MORBs have K/Cl ratios about twice those of N-MORBs at a given δ^{37}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 δ^{37}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 δ^{37}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 (~34; see diamonds in Fig. 2), but N-MORB sources are lower in δ^{37}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 δ^{37}Cl value of –1.6‰ or less, which is lower than values previously proposed (*9*, *10*). The different value of Magenheim *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 δ^{37}Cl and low nominal Cl contents, which is incompatible with the δ^{37}Cl-1/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 $Na_{8.0}$, K/Ti, K/Cl, and spreading rate) would yield the simple δ^{37}Cl-1/Cl trend that we found if low-Cl, high-δ^{37}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 δ^{37}Cl value unmodified by contamination is $\leq$ –1.6‰, which is significantly more negative than that of the surface reservoirs (~0‰). This isotopic difference might result from (i) systematic ^{37}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}Cl enrichment of the surface Cl of early Earth due to a late supply of volatile-rich material (*30*), which was enriched with ^{37}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 δ^{37}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 δ^{37}Cl (preliminarily estimated from serpentinites, average δ^{37}Cl = –0.7 ± 0.4‰) (*11*) than the mantle flux (δ^{37}Cl $\leq$ –1.6‰); such a combination of fluxes could only have decreased the δ^{37}Cl gap between mantle and surface reservoirs over the long-term exchanges.

References and Notes

1. A. Jambon, B. Déruelle, G. Dreibus, F. Pineau, *Chem. Geol.* **126**, 101 (1995).
2. P. J. Michael, W. C. Cornell, *J. Geophys. Res.* **103**, 18325 (1998).
3. A. E. Saal, E. H. Hauri, C. H. Langmuir, M. R. Perfit, *Nature* **419**, 451 (2002).
4. Chlorine stable isotope compositions are expressed as $\delta^{37}\text{Cl} = \{[(^{37}\text{Cl}/^{35}\text{Cl})\text{sample}/(^{37}\text{Cl}/^{35}\text{Cl})\text{SMOC}] - 1\} \times 1000$, where SMOC is standard mean ocean chloride, defined as 0‰.
5. R. Kaufmann, A. Long, H. Bentley, S. Davis, *Nature* **309**, 338 (1984).
6. A. Godon *et al*., *Chem. Geol.* **207**, 1 (2004).
7. H. G. M. Eggenkamp, R. Kreulen, A. F. Koster Van Groos, *Geochim. Cosmochim. Acta* **59**, 5169 (1995).
8. C. J. Eastoe, T. M. Peryt, O. Y. Petrychenko, D. Geisler-Cussey, *Appl. Geochem.* **22**, 575 (2007).
9. A. J. Magenheim, A. J. Spivack, P. J. Michael, J. M. Gieskes, *Earth Planet. Sci. Lett.* **131**, 427 (1995).
10. Z. D. Sharp *et al*., *Nature* **446**, 1062 (2007).
11. M. Bonifacie *et al*., *Geochim. Cosmochim. Acta* **72**, 126 (2008).
12. Z. D. Sharp, J. D. Barnes, *Earth Planet. Sci. Lett.* **226**, 243 (2004).
13. M. Bonifacie *et al*., *Geochim. Cosmochim. Acta* **69**, A787 (2005).
14. J. D. Barnes, Z. D. Sharp, *Chem. Geol.* **228**, 246 (2006).
15. M. Bonifacie *et al*., *Chem. Geol.* **242**, 187 (2007).
16. A. Godon *et al*., *Geochim. Cosmochim. Acta* **68**, 2153 (2004).
17. M. Bonifacie, C. Monnin, N. Jendrzejewski, P. Agrinier, M. Javoy, *Earth Planet. Sci. Lett.* **260**, 10 (2007).
18. V. Woulé Ebongué, N. Jendrzejewski, F. Walgenwitz, F. Pineau, M. Javoy, *AAPG Bull.* **89**, 1005 (2005).
19. Materials and methods are available as supporting material on *Science* Online.
20. P. J. Michael, J.-G. Schilling, *Geochim. Cosmochim. Acta* **53**, 3131 (1989).
21. S. A. Soule *et al*., *Earth Planet. Sci. Lett.* **252**, 289 (2006).
22. J.-G. Schilling, M. B. Bergeron, R. Evans, *Philos. Trans. R. Soc. London Ser. A* **297**, 147 (1980).
23. P. Richet, Y. Bottinga, M. Javoy, *Annu. Rev. Earth Planet. Sci.* **5**, 65 (1977).
24. H. P. Schauble, G. R. Rossman, H. P. Taylor Jr., *Geochim. Cosmochim. Acta* **67**, 3267 (2003).
25. C. K. Unni, J.-G. Schilling, *Nature* **272**, 19 (1978).
26. J. D. Webster, R. J. Kinzler, E. A. Mathez, *Geochim. Cosmochim. Acta* **63**, 729 (1999).
27. M. Bonifacie, J. L. Charlou, N. Jendrzejewski, P. Agrinier, J. P. Donval, *Chem. Geol.* **221**, 279 (2005).
28. C. H. Langmuir, E. M. Klein, T. Plank, in *Mantle Flow and Melt Generation at Mid-Ocean Ridges*, J. Phipps-Morgan, D. K. Blackman, J. M. Sinton, Eds. (American Geophysical Union, Washington, DC, 1992), vol. 71 of Geophysical Monograph Series, pp. 183–280.
29. C. M. Meyzen, M. J. Toplis, E. Humler, J. N. Ludden, C. Mével, *Nature* **421**, 731 (2003).
30. M. Javoy, *Chem. Geol.* **147**, 11 (1998).

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Materials and Methods
Figs. S1 and S2
Tables S1 and S2
References

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Supporting Online Materials for

“The Chlorine Isotope Composition of Earth’s Mantle”

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Supporting Online Material

Materials and Methods

Figs. S1 and S2 + legends

Table S1 and S2 + legends

Supporting References

Materials and Methods

Descriptions of the whole analytical procedure used for measuring Cl contents and isotopic compositions of silicate samples and the experiments run for its validation have been detailed and validated in a previous publication (*S1*) and are only summarized herein. The main steps of the procedure consist of chlorine extraction from powdered samples by pyrohydrolysis and chloride conversion to CH_3Cl_{gas} for isotope ratio determination by gas-source, dual-inlet mass spectrometry.

Sample preparation

Prior to crushing, centimeter size pieces of fresh glass are sonicated at least twice in filtered-deionised High-Performance Liquid Chromatography (HPLC) quality water. This step avoids any contamination due to sample collection, handling or preparation. Perfect pieces of glass from the 200-400 μm fraction are hand-picked under a binocular microscope before the fine crushing step in order to avoid any contamination from altered material. After cleaning in deionized water and drying, selected fragments are crushed and grounded to a grain size of less than 160 μm. The resulting powder is dried in a closed oven at atmospheric pressure at 80°C for at least 6 hours.

Extraction of structural-chlorine from silicates by pyrohydrolysis

The powdered sample is intimately mixed in a platinum boat with 5 to 6 times its weight of vanadium pentoxide (V_2O_5), used as a flux. The Pt boat is placed in the centre part of a silica tube heated at 1200°C by a resistance furnace. A nebuliser produces a fine aerosol spray of pure water instantaneously converted to vapour inside the tube. Dried air and water vapor carry extracted analytes (including halogens) that are recovered by bubbling into a collecting flask containing a NaOH solution (0.1M). Prior to each sample extraction, a complete extraction without the V_2O_5 /sample mixture is run at 1250°C to clean the whole apparatus.

Cl-content determination

An aliquot of the pyrohydrolysis solution is reserved for the HPLC determination of Cl content. Cl content of the neutralized aliquot is determined by comparison with five standard solutions with Cl concentrations in the range defined by samples. The accuracy of Cl content determination by HPLC is estimated to be better than 5%. Cl concentration of the pyrohydrolysed sample is calculated on the basis of HPLC measurements and the mass of sample fused. This calculated Cl concentration is compared to the recommended value determined by electron microprobe.

Cl contents of polished sections of glass were determined with a Cameca SX100 electron microprobe at the CAMPARIS centre (Paris 6 University, France). The analytical conditions used are 15 kV accelerating voltage, 100 nA sample current, 20 μm beam size, 400 s counting time for one point (*S2*). At least six spots were analyzed on each polished section and a mean value calculated to average out heterogeneity effects. Results were corrected using a calibration based on international reference samples (JDF2, TR154-21D-3, EN112-7D-13 and TR138-6D-1, analyzed in (*S2*)).

δ^{37}Cl Measurements

In the pyrohydrolysis solution, chlorine from the sample is in chloride form, which is then converted into CH_3Cl_{gas} and purified from excess $CH_3\,I_{gas}$ following the method described by (*S3*) and (*S4*). This method has been cross-calibrated with three other laboratories (*S5*). Seawater aliquots of laboratory reference material, *Atlantique 2* (North Atlantic Ocean, 36°43'N and 11°36'N; (*S5*)) were prepared and treated as and with the sample solutions. The seawater volumes used cover the range of Cl content pyrohydrolysed MORB samples analyzed the same day. Seawater aliquots are analyzed isotopically against the reference gas before and after each batch of typically two MORB samples analyzed. This procedure checks for instrumental drift during the day, and allows direct comparison between the sample and the seawater reference. The isotopic composition of the sample is compared to the daily average of isotopic compositions of seawater aliquots of size comparable to the MORB sample size, to make a correction for the CH_3Cl conversion/purification blank and for the instrumental background (mainly the gas chromatograph and the mass spectrometer). δ^{37}Cl measurements were performed on CH_3Cl_{gas} using triple collector dual-inlet mass spectrometers: a VG Optima and a Finnigan Delta Plus XP at Paris (Laboratoire de Géochimie des Isotopes Stables, IPGP/Paris 7 University, France) and a VG Sira 12 at

Reading (Post-graduate Research Institute for Sedimentology - PRIS, Reading University, UK). There are no significant differences between δ^{37}Cl results for seawater and the internal rock-reference sample (SO100DS92: fresh andesite glass from the Pacific-Antarctic Ridge with 9042 ppm Cl) run in Reading or Paris.

Validation and statistical characteristics of the whole-procedure used in this study

In the absence of international rock reference materials for δ^{37}Cl measurements, we were particularly careful to check blanks, extraction yields (Cl extracted compared to recommended Cl contents), CH_3Cl conversion yields (converted CH_3Cl is quantified with a calibrated pressure gauge after CH_3I purification and compared to recommended Cl contents) and reproducibilities on both Cl and δ^{37}Cl measurements. Notably, various amounts of the internal reference sample SO100DS92 (~ 2 to 60 μmol of Cl equivalent) have been pyrohydrolysed and analyzed (Table S2). Accurate isotopic determinations require: (i) quantitative recovery of chlorine during pyrohydrolysis and CH_3Cl conversion to avoid possible isotope fractionation, and (ii) no contamination by a Cl-rich material during both of these steps. To our knowledge, no previous δ^{37}Cl study of Cl-poor igneous rocks has consistently demonstrated quantitative analytical yields and evaluated the whole-method blanks.

Extraction yields

The quality of the pyrohydrolysis extraction was checked on three Cl-content international reference materials from the Geological Survey of Japan (GSJ) and two laboratory glass standards (including SO100DS92) with Cl contents between 39 and 9042 ppm (*S1*). The Pyrohydrolysis/HPLC method leads to overall Cl extraction yields of 100 ± 8% (1σ). Following Eggenkamp's recommendation and our own experience, only analyses with yields between 85 and 115% should be considered reliable. We believe that heterogeneity of natural samples, uncertainties in the recommended Cl-contents and the HPLC 5% uncertainties can account for most of this observed yield range.

Whole-procedure blanks

Pyrohydrolysis blanks are lower than 0.5 μmol, corresponding to less than 16 wt% of the sample chloride analyzed in this study for the lowest Cl samples (and generally much less for higher-Cl samples, the average blank for all samples is typically 7%). Moreover, the fact that all samples of varying Cl concentrations (between 39 and 9042 ppm) show similar yields also argues in favor of a low pyrohydrolysis blank (*S1*). In terms of Cl-concentations, the pyrohydrolysis blank has no significant effect even for small amounts of Cl extracted from SO100DS92 (see Fig. S1a).

As the Cl whole-procedure blank (including powdering the samples and their handling, pyrohydrolysis and CH_3Cl preparation/purification) is much below the minimum amount required for δ^{37}Cl measurements by dual-inlet mass spectrometry (~ 2 μmole), its δ^{37}Cl signature had to be estimated indirectly. The method adopted consists in evaluating the effect of the whole-procedure blank on extractions/analyses of various amounts of the reference rock SO100DS92 (equivalent to 2 to 59 μmoles of Cl). The fact that there is no correlation between the δ^{37}Cl determination and the amount of laboratory reference material fused (Fig. S1b) or Cl extraction yields (Fig. S1c) shows that the whole-procedure blanks have only small effects on the determination of the δ^{37}Cl value of the reference rock. Therefore, the whole-procedure blanks have δ^{37}Cl values close to that of SO100DS92 (ca. -0.5‰). Interval estimation with Monte Carlo simulation based on data from repeated extractions/analyses of different amount of SO100DS92 suggests that our analytical blank has a δ^{37}Cl value of -0.3 ± 2.2‰ (95% probability) (Fig. S2).

Uncertainties on δ^{37}Cl measurements for silicate samples

During the course of this study, the mean reproducibility on internal reference seawater *Atlantique 2* (see ref. (S5) for details) was ± 0.12‰ (1σ) for 50 analyses. The external precision of the whole method for the δ^{37}Cl determination of structural chlorine from silicate samples, estimated through replicate analyses of SO100DS92, is ± 0.14‰ (n=15; 1σ; Table S2).

Potential effect of an analytical blank on MORB δ^{37}Cl measurements

We can test whether the δ^{37}Cl vs. 1/Cl relationship observed in Fig. 1 results from contamination by an analytical blank of less than 0.5 μmole (maximum measured blank). The mixing hyperbola for MORB samples (equivalent to the the linear relationship in Fig. 1) and its upper and lower 95% confidence limit curves are shown in Fig. S2. This set of curves cuts the upper limit of measured blank size (0.5 μmole) for δ^{37}Cl values between -5.5 and -14.1 ‰, indicating that δ^{37}Cl value of the potential blank should be in this range to explain the δ^{37}Cl vs. 1/Cl relationship for MORB samples. This range does not match that determined by repeat extraction/analyses of the reference-rock SO100DS92 (n = 15), which instead define a blank ranging from ~ -2.5 to 2‰ (Fig. S2). Therefore it is highly unlikely that our analytical blank can explain the δ^{37}Cl-1/Cl relationship seen in Fig. 1.

Supporting Online Figures and Tables

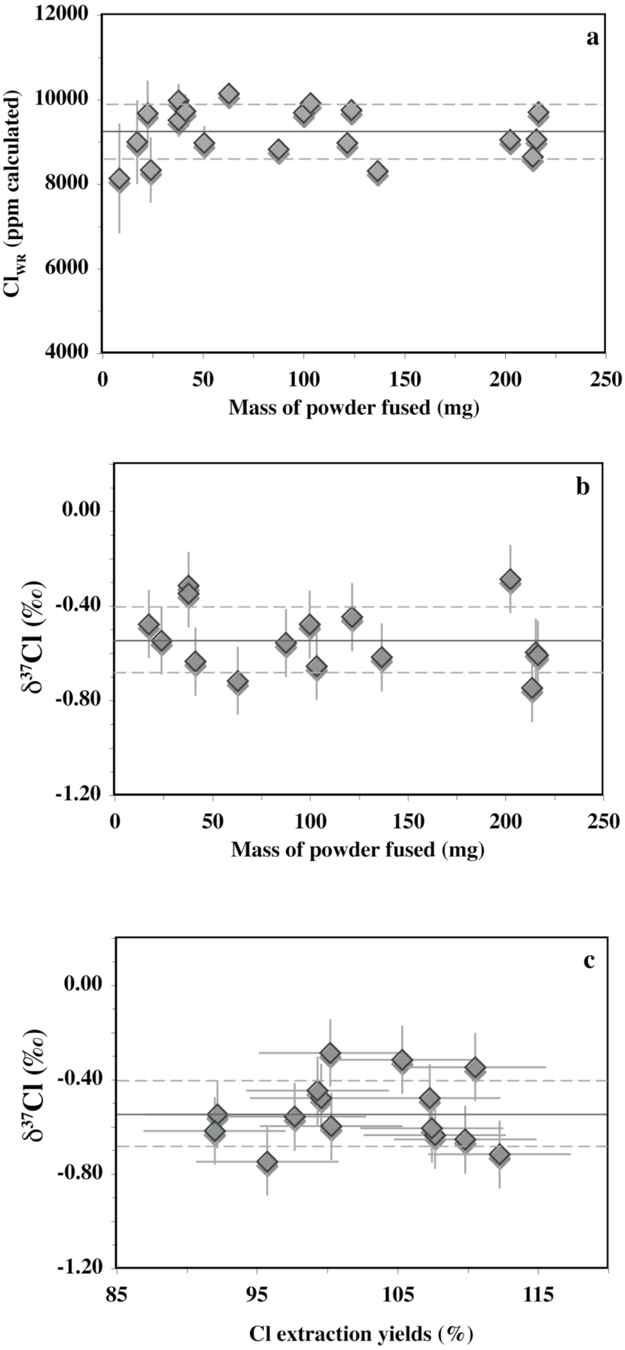

Fig. S1. Replicate analyses of our internal reference material SO100DS92. **a.** Cl content of the whole-rock (calculated after HPLC measurement) compared with the amount of internal reference fused. **b.** Chlorine isotopic composition versus mass of powder fused. **c.** Chlorine isotopic compositions versus extraction yields.

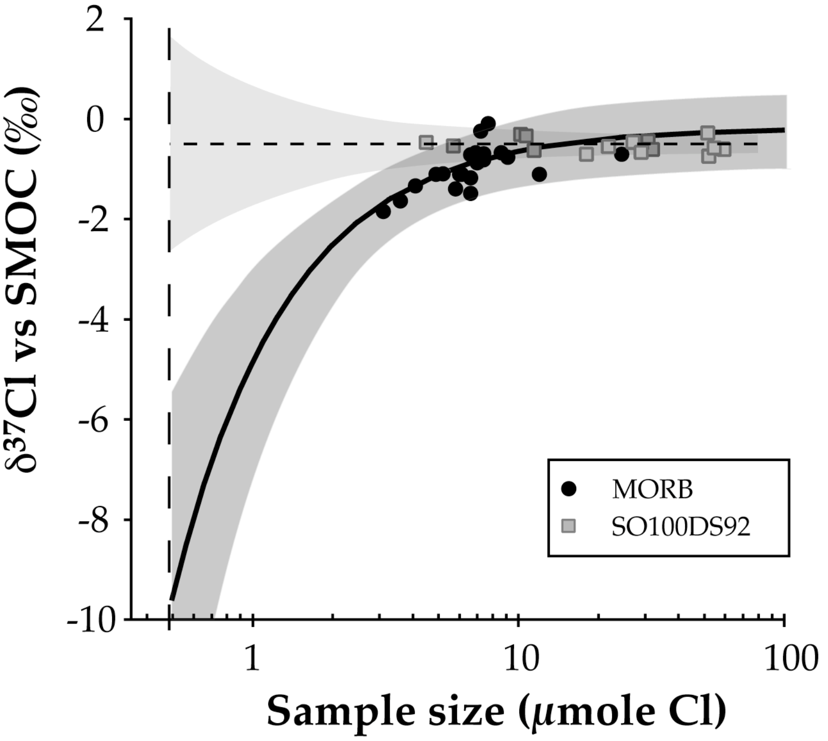

Fig. S2. Comparison of the mixing hyperbola for MORB data (n = 22; black circles) from this study (black curve) and its 95% confidence limits (dark grey) with the mixing hyperbola (dashed horizontal line) and its 95% confidence limits (light grey) defined for blank by repeat analyses of the reference-rock SO100DS92 (n = 15; grey squares). Uncertainties on MORB and SO100DS92 data are within the symbol size. The vertical dashed line is the upper limit of the measured blank (0.5 *μ*mole).

Sample Name	Ridge	Depth mbsl	Spr. Rate mm.yr^{-1}	MgO wt.%	Na$_{8.0}$ wt.%	K/Ti	K/Cl	n/n	Cl ppm	± 1σ	δ^{37}Cl ‰
Normal-MORB											
SR2-DR03	EPR	2800	153	6.9	2.8	0.05	3.2	3/1	184	16	-0.8
SR2-DR04	EPR	2790	153	6.9	3.0	0.06	1.3	1/1	461	37	-0.7
CY84-30-06	EPR	-	95	7.0	2.6	0.10	7.4	2/2	145	1	-1.1
SR1-DR04	EPR	2900	120	7.0	2.6	0.12	10.0	1/1	149	21	-0.7
CLIPP-DR01-1	EPR	2610	95	7.9	3.0	0.13	14.2	2/2	70	11	-1.1
SR1-DR03	EPR	2650	95	7.5	3.0	0.14	11.1	1/1	150	20	-1.1
SO22-29D	GSC	2580	58	6.6	2.2	0.05	1.2	2/2	426	33	-0.3
SO22-20D	GSC	2750	58	6.0	2.1	0.05	1.5	2/1	429	30	-0.8
SO22-17D	GSC	2580	58	5.9	1.9	0.06	1.0	1/1	701	50	-0.1
MD57-D9-1	CIR	3710	35	8.2	2.9	0.04	5.0	1/1	50	10	-1.4
MD57-D7-2	CIR	3470	37	7.5	2.9	0.11	21.7	1/1	42	7	-1.9
EDUL-DR57-1-2	SWIR	4100	16	9.2	3.6	0.05	9.2	1/1	45	10	-1.5
Average N-MORB	*-1.0 ± 0.5 ‰*										
Enriched-MORB											
CY 82-27-01	EPR	2665	95	7.3	2.9	0.17	14.8	3/2	123	11.5	-0.7
CY82-18-01	EPR	2700	95	7.5	3.0	0.15	18.5	1/1	94	19	-0.7
SR1-DR02	EPR	2750	83	6.5	2.7	0.18	11.6	3/1	157	15	-0.9
CY 82-09-03	EPR	2630	95	7.5	3.0	0.33	35.7	2/1	100	9	-1.2
CH97-DR-02	MAR	1800	25	7.7	2.1	0.37	8.6	3/1	320	22	-0.7
EW9309-41D-1g	MAR	3520	30	7.9	2.7	0.15	24.2	1/1	55	12	-1.1
EW9309-9D-1g	MAR	3892	30	6.9	2.9	0.41	33.8	2/2	130	14	-1.1
EDUL-DR-8-1-2	SWIR	4905	16	7.9	4.2	0.20	33.2	2/2	55	10	-1.3
SWIFT-DR-6-1-1	SWIR	2300	15	6.7	3.0	0.27	11.8	1/1	260	38	-0.8
EDUL-DR-29-3-2	SWIR	3550	16	7.9	4.2	0.24	38.3	1/1	52	10	-1.6
Average E-MORB	*-1.0 ± 0.3‰*										

Table S1- Cl content and isotopic compositions of MORB glasses. Normal and enriched mid-oceanic ridge basalts are classified on the basis of their K/Ti ratios (< 0.15 and ≥ 0.15, respectively). MAR= Mid-Atlantic Ridge; EPR= East Pacific Rise; GSC= Galapagos Spreading Center; SWIR= South-West Indian Ridge; CIR= Central Indian Ridge. mbsl= meter below sea level; Spr. R.= full spreading-rate of the corresponding segment (*S6*). $Na_{8.0}$= Na_2O corrected for crystal fractionation to 8% MgO. K/Ti and K/Cl are wt. % ratios. $Na_{8.0} = [Na_2O+0.115*(8-MgO)]/[1+0.133*(8-MgO)]$ (*S7*). n/n= number of extractions and number of δ^{37}Cl analyses run for each sample. Major elements concentrations were determined by electron microprobe at the CAMPARIS centre. Cl contents reported are calculated based on HPLC analyses (*19*) of the pyrohydrolyzed solution; Cl uncertainties (1σ) represent analytical variations and/or sample heterogeneities. During the course of this study, the mean reproducibility of δ^{37}Cl measurement was ± 0.12‰, 1σ, determined on 50 analyses of the internal reference seawater *Atlantique 2* (*S5*). Most MORB samples were extracted and analyzed twice: repeat analyses showed identical δ^{37}Cl values within the ± 0.14‰ external uncertainty of the whole-procedure for silicate analyses, determined on repeated extraction/analyses of our internal rock-reference SO100DS92 (Table S2).

Mass (mg)	Cl $_{WR}$ (ppm)	Yields (%)	δ^{37}Cl (‰)	Lab.
9	8114	90	-	-
18	8975	100	-0.48	P1
23	9655	107	-	-
24	8310	92	-0.55	P2
38	9496	105	-0.32	P2
38	9962	111	-0.35	P2
42	9704	108	-0.64	P2
51	8954	99	-	-
63	10120	112	-0.72	P2
88	8805	98	-0.56	P1
100	9670	107	-0.48	P2
104	9899	110	-0.66	P2
122	8952	99	-0.45	P1
124	9731	108	-	-
137	8292	92	-0.62	R
203	9033	100	-0.29	P1
214	8629	96	-0.75	P2
216	9039	100	-0.60	P1
217	9685	107	-0.61	P1

Table S2- Results of repeat analyses of the SO100DS92 internal reference glass. Mass: mass of powder fused; Cl_{WR}: Cl content of the whole rock = 35.5 (g/mol)*number of Cl μmoles extracted (measured by HPLC) * 1000 / Mass (mg). Yields: extraction yields = 100 * Cl_{WR} / 9010 (recommended Cl for SO100DS92); Lab: laboratory/mass spectrometers on which δ^{37}Cl data have been determined: R stands for Reading and VG Sira 12; P1 stands for Paris and VG

Optima; P2 stands for Paris and Finnigan Delta plus XP. n.d.: not determined. Mean δ^{37}Cl value for 19 extractions and 15 δ^{37}Cl analyses is - 0.54 ± 0.14‰ (1σ).

Supporting Online References

S1. M. Bonifacie *et al.*, *Chem. Geol.* **242**, 187 (2007).

S2. P. J. Michael, W. C. Cornell, *J. Geophys. Res.* **103**, 18325 (1998).

S3. A. Long *et al.*, *Geochimica et Cosmochimica Acta* **57**, 2907 (1993).

S4. H. G. M. Eggenkamp, Ph. D. Thesis, Utrecht University (1994).

S5. A. Godon *et al.*, *Chem. Geol.* **207**, 1 (2004).

S6. C. DeMets, R. G. Gordon, D. F. Argus, S. Stein, *Geophys. J. Int.* **101**, 425 (1990).

S7. C. H. K. Langmuir, E. M. Klein, T. Plank, in *In Mantle flow an Melt generation at Mid-Ocean Ridges* J. P. *e. a.* Morgan, Ed. (AGU Monograph, Washigton D.C., 1992), vol. 71, pp. 183-280.