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Halogen enrichment on the continental surface: a perspective from loess

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Abstract

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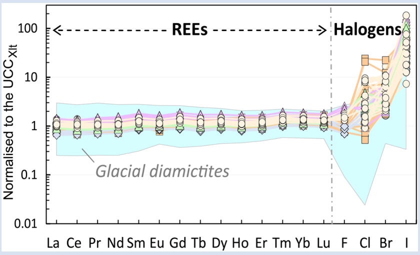

Halogen (F, Cl, Br, and I) concentrations for 129 loess samples from worldwide localities yield geometric means of 517 ± 53 μg/g F, 150 ± 20 μg/g Cl, 1.58 ± 0.16 μg/g Br, 1.16 ± 0.11 μg/g I (2 standard errors). These concentrations, notably for Br and I, are substantially higher than previous estimates for the average upper continental crystalline bedrocks, with enrichment factors of $1.3^{+0.7}_{-0.4}$ (F), $1.8^{+2.4}_{-0.8}$ (Cl), $3.8^{+1.3}_{-1.0}$ (Br), and 39^{+71}_{-16} (I) (95 % confidence), documenting enrichment of halogens on the continental surface. These surface halogens are likely sourced from the oceans and may be influenced by climate fluctuations. Halogen ratios (Br/Cl, I/Cl, and Br/I) in loess are similar to those of organic-rich soils/sediments from both terrigenous and marine settings, suggesting that terrigenous and marine organic matter have indistinguishable halogen ratios. The Br/I ratios differ from those in the fine grained matrix of glacial diamictites, indicating that another process (beyond biological influence) is responsible for fractionating halogens in the upper continental crust. Using a mixing model, we calculate that over 80–90 % of loess originates from crystalline bedrocks, while the remainder (<10–20 %) derives from the halogen- and organic-rich sedimentary cover or other sources (*e.g.,* marine aerosols).

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Introduction

Halogens (F, Cl, Br, and I), an important group of lithophile and volatile elements, are primarily concentrated in Earth's surface reservoirs (*e.g.,* crust, seawater, and sediments) and play a critical role in modulating Earth's habitability (Kendrick, 2024 and references therein). To quantify the halogen cycle operating on Earth, it is necessary to have an accurate estimate of halogen distributions in different terrestrial reservoirs. However, such estimates are still lacking for much of the continental crust. This lack of knowledge regarding the geochemical behaviour of halogens during terrestrial geological processes, such as chemical weathering, metamorphic dehydration, and geobiological activity, limits our understanding of the role of the continental crust in the global halogen cycle, and also hinders our ability to utilise halogen concentrations and elemental ratios to trace geologic processes (Hanley and Koga, 2018).

To date, there are only five independent estimates of halogen concentrations in the upper continental crust (UCC), and these estimates can differ by up to a factor of ~50 (Shaw *et al.,* 1967; Wedepohl, 1995; Gao *et al.,* 1998; Muramatsu and Wedepohl, 1998; Han *et al.,* 2023). Poorly constrained halogen concentrations in continental rocks are partly due to heterogeneous halogen distributions, and partly due to the analytical challenges of obtaining precise and accurate halogen concentrations at low abundances, especially for Br and I. With recent advances in analytical techniques, Han *et al.* (2023) reported a comprehensive set of high quality F-Cl-Br-I data for 24 composite samples of the fine grained matrix of ancient glacial diamictites, considered a proxy for upper continental crust (Gaschnig *et al.,* 2016), and used these data to derive halogen estimates for the crystalline and weathered UCC. However, because the diamictites record chemical weathering in their provenance, the new estimates may represent minima for the crystalline UCC (Han *et al.,* 2023). Moreover, significant fractionation of Br/Cl and I/Cl ratios is observed in the glacial diamictites relative to pelagic sediments, and the reasons for this are unknown. These differences may reflect organic matter enrichment in the sea floor sediments relative to the UCC, chemical weathering of the UCC, or the effects of diagenesis/metamorphism on the diamictites (Han *et al.,* 2023). To better constrain the average halogen composition of the continental surface and to explore the mechanism(s) responsible for the fractionation of halogen ratios in sediments, we analysed 129 loess samples from worldwide localities.

Loess is a silt-sized, terrestrial aeolian sediment that covers about 10 % of the continental surface (Pye, 1995). Previous studies have used loess as a proxy for the average composition of the UCC because of its wide scale sampling of the continental surface, limited chemical weathering (compared to shales) and minor mineralogical and elemental fractionation during sedimentary transportation and deposition (*e.g.,* Taylor *et al.,* 1983; Gallet *et al.,* 1998; Chauvel *et al.,* 2014; Sauzéat *et al.,* 2015). However, previous research on loess mainly focused on

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insoluble elements like rare earth elements, with little attention paid to halogens. Only two previous studies have reported halogen concentrations in loess, each focusing on just one or two halogens (F and Cl by Liu *et al.*, 1981; I by Fan *et al.*, 2021) in loess-palaeosol profiles to track palaeoclimate. Thus, there have been no systematic studies of the behaviour of halogens in loess. Here, we report F-Cl-Br-I concentrations, along with major and rare earth element abundances, for 129 loess samples from Germany, Switzerland, the United States, Argentina, Kazakhstan, and China (Table S-1 and Fig. S-1), and discuss the behaviour of halogens on the continental surface and implications for global halogen recycling.

Halogen Concentrations and Mineralogical Hosts in Loess

Halogen concentrations were analysed by two methods: (1) combustion ion chromatography analysis (C-IC) for F, and (2) NH_4HF_2 digestion and ICPMS analysis (N-ICPMS) for Cl, Br, and I (Supplementary Information). Halogen concentrations of loess are reported in Table S-1 and plotted in Figure 1. Each halogen has distinctive geochemical properties, making each likely to be controlled by different phases in loess. Loess is mainly composed of quartz, feldspar, and various amounts of phyllosilicates and carbonates (Pye, 1995). Fluorine, with the smallest anionic radius of the group, may readily replace the hydroxyl anion and be incorporated into phyllosilicates. This is supported by a good correlation between F and Al_2O_3 ($R^2 = 0.84$) and K_2O ($R^2 = 0.78$) in loess, the latter two elements being enriched in phyllosilicates (Fig. 2a,b). Another mineral in loess capable of hosting F is carbonate, as two F^- can substitute for CO_3^{2-} (Feng *et al.*, 2021). However, F and CaO show a slight negative correlation (Fig. S-3), suggesting that F in loess is mainly controlled by phyllosilicates, rather than carbonates. The anti-correlation between F and CaO contrasts with the relatively high F content observed in some marine carbonates (Rude and Aller, 1991). The reason for a lack of carbonate control on F in the loess is unclear but may indicate that F substitution within carbonate occurs only in certain geological environments, which, in turn, might relate to the salinity, $p\mathrm{CO}_2$, and/or temperature of the water body from which the carbonates precipitate (*e.g.*, Rude and Aller, 1991; Ramos *et al.*, 2005; Feng *et al.*, 2021).

The increasing anionic radii of Cl, Br, and I compared to F make them less likely to be incorporated into the crystal lattices of silicate minerals, particularly for Br and I. Instead, they may be absorbed on mineral surfaces or concentrated in fluid inclusions, evaporite minerals, and/or organic matter. We conducted a leaching experiment with MilliQ water on 14 samples to determine the location of these elements in loess (Table S-1 and Fig. S-4). The water soluble component of halogens in loess gradually decreases from Cl (as high as ~85 %) to Br (~50 %), to I (~25 %) (Fig. S-4), suggesting that most of the Cl in loess exists in soluble form, while Br and I are mainly present in water-insoluble phases. The soluble halogens in loess (Cl and Br) may originate from a range of sources: (1) soluble inorganic halogens incorporated or absorbed onto the silicate phases

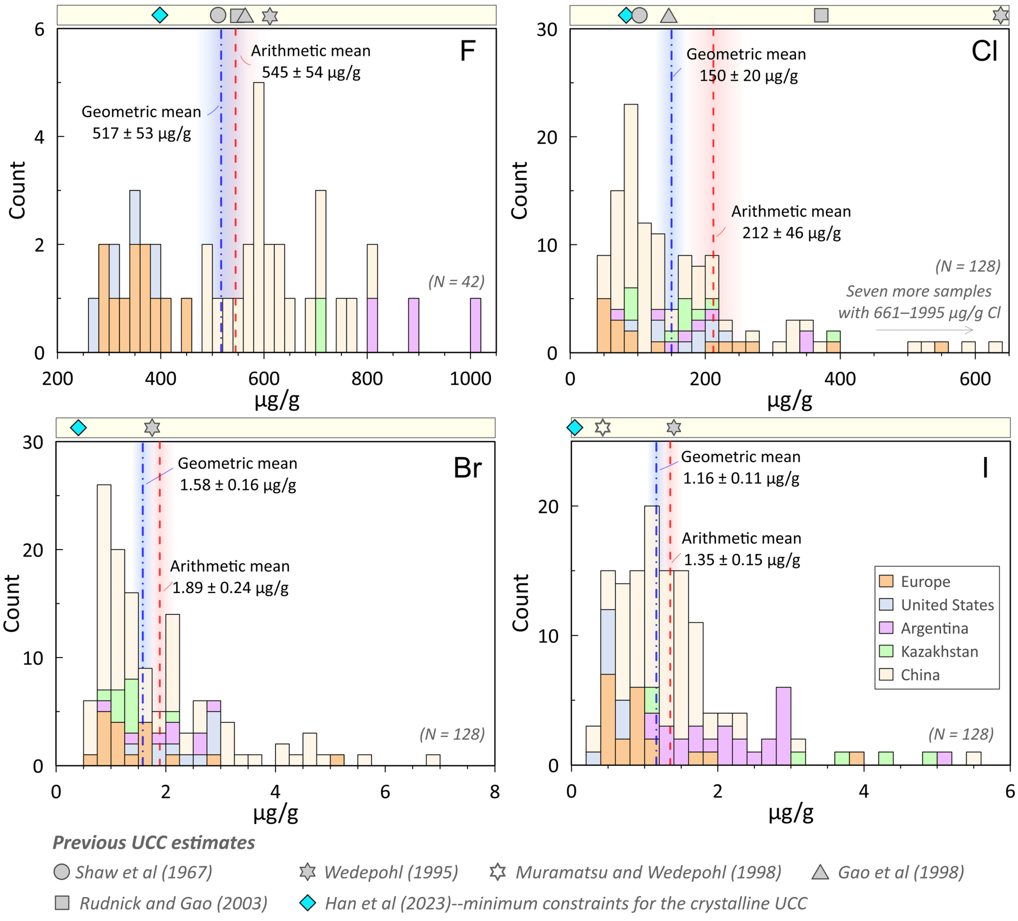

Figure 1 Halogen (F, Cl, Br, and I) concentrations of loess samples. The blue dash-dotted and the red dashed lines represent the geometric and arithmetic means of the loess data set, respectively, along with uncertainties of 2 standard errors (s.e., light-shaded bars; see Fig. S-5 for more details on the calculation). Symbols above each histogram represent previous estimates of halogen abundances in the UCC.

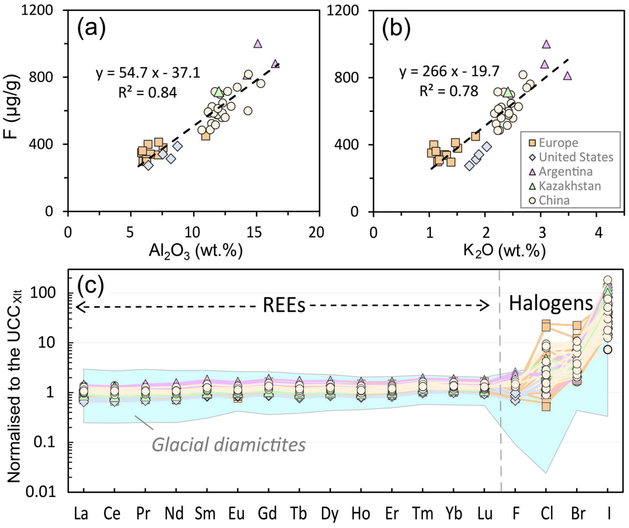

Figure 2 Fluorine *versus* **(a)** Al_2O_3 and **(b)** K_2O contents of loess. **(c)** Normalised rare earth element (REE) and halogen concentrations of loess samples relative to the composition of the crystalline UCC (UCC_{Xlt}): REE estimates for UCC are from Rudnick and Gao (2003) and halogens are from Han *et al.* (2023). The cyan-shaded area shows the compositional field of glacial diamictite composites.

within loess source materials, (2) soluble halogens in organic matter, (3) evaporite minerals like halite, and (4) post-depositional contamination from either anthropogenic sources and/or meteoric/ground water. The first three sources may reflect halogen distributions on the continental surface when loess deposits formed, while the fourth suggests potential disturbances of halogen contents after deposition. Since no significant regional differences are observed in the Cl and Br contents of samples from different areas (Fig. 1), and considering that their concentrations in meteoric water and groundwater are typically 10–100 times lower than those of loess (Worden, 2018), any enrichment from localised post-depositional processes, if they occurred, is likely minimal.

The concentrations of residual Br and I (after leaching) in loess are significantly higher than their averages in glacial diamictites (Fig. S-4). Because both elements have a strongly biophilic affinity, they may primarily be hosted in organic matter. Loess contains a significantly greater amount of organic matter than crystalline bedrocks, which are the main source of glacial diamictites (Han *et al.*, 2023). A possible reason for this difference might be the colder environment prevailing during the formation of glacial diamictites, leading to lower biomass on land surfaces and consequently less enrichment of halogens in the diamictites. This explanation also aligns with the proposition put forward by Fan *et al.* (2021) regarding climate fluctuations and I content in loess: in warmer periods, more halogens will be transported from the ocean to land and retained by surface biota, while during colder periods, both halogen transport efficiency and retention on land will decrease. In other words, halogen concentrations in terrigenous sediments, particularly for the less soluble Br and I, may be used as a proxy to monitor past temperature changes and to trace patterns of halogen movement between land and sea.

As a whole, the geometric and arithmetic means calculated from the data set are systematically higher than the recent estimates for crystalline UCC derived from data for ancient glacial diamictite composites (Han *et al.*, 2023). Using a bootstrap approach, we estimate the degree of halogen enrichment in loess relative to crystalline UCC to be $1.3^{+0.7}_{-0.4}$ times for F, $1.8^{+2.4}_{-0.8}$ times for Cl, $3.8^{+1.3}_{-1.0}$ times for Br, and 39^{+71}_{-16} times for I (95 % confidence, see Fig. S-6), with an exponential increase in enrichment from F to I (*i.e.* $F < Cl < Br << I$; Fig. 2c and Fig. S-7). There are two non-mutually exclusive factors that could explain the higher halogen contents in loess relative to glacial diamictites: (1) a lower degree of chemical weathering in the provenance of loess compared to that of glacial diamictites, and (2) greater potential for incorporation and preservation of organic matter in loess than in glacial diamictites (Fig. S-8). On the other hand, the mean halogen concentrations in loess are comparable to previous estimates of halogens in the UCC based on either large scale sampling (Shaw *et al.*, 1967; Gao *et al.*, 1998) or models based on lithologies (Wedepohl, 1995; Muramatsu and Wedepohl, 1998) (Fig. 1), both of which incorporate data not only for crystalline bedrocks, but also for many halogen-rich lithologies such as shales, carbonates, and evaporites from the overlying sedimentary cover. The similarity between mean halogen concentrations in loess and these previous estimates suggests that halogens in loess may provide a useful average of halogen concentrations across various types of rocks and sediments at the continental surface. Halogen enrichment on the continental surface may derive from the oceans, a major halogen reservoir (Hanley and Koga, 2018), with halogen fluxes from oceans to continents potentially regulated by climate fluctuations, as suggested by Fan *et al.* (2021).

Halogen Ratios in Loess

The Br/Cl and I/Cl ratios of loess, as well as the leached residues of loess samples, are significantly fractionated relative to those in igneous rocks like MORB/OIB and arc/backarc lavas, closely tracking the compositional range seen in pelagic sediments, whose halogen concentrations are primarily controlled by marine organic matter (John *et al.*, 2011) (Fig. 3). This supports the inference above, based on leaching experiments (Fig. S-4), that Br and I primarily reside in water-insoluble organic matter in loess. It also suggests that both terrigenous and marine organic matter have indistinguishable halogen ratios. This notion is further supported by the consistently narrow range of the Br/I ratio observed in organic-rich soils and sediments from Japan (Yamasaki *et al.*, 2015) and China (He *et al.*, 2018) (Fig. S-9). However, no correlation is observed between Br (or I) and TOC in either the loess or Japanese soil samples (Fig. S-10), which is somewhat counterintuitive and may result from varying Br/TOC (or I/TOC) ratios in different types of organic matter (Muramatsu and Wedepohl, 1998; Mayer *et al.*, 2007). Therefore, great caution should be exercised when using the correlation of Br and I with TOC to infer the presence of organohalogens in sediments.

The halogen ratios observed in loess are also similar to those found in blueschists and serpentinites from subduction zone settings (Fig. 3), indicating that the halogens in these metamorphic rocks may be overprinted by fluids derived from subducted terrigenous organic-bearing sediments, not just marine sediments (*e.g.*, John *et al.*, 2011; Kendrick *et al.*, 2013; Pagé *et al.*, 2016). Most glacial diamictite composites (excluding five carbonate and terrigenous sediment-rich samples from Namibia), however, have significantly higher Br/I ratios (7–74) compared to loess (0.25–6.3) (Fig. 3). This difference suggests that halogen ratios are significantly fractionated within the upper continental crust by an additional process, such as continental weathering and/or diagenesis/metamorphism. We note that the diamictites generally carry a stronger chemical weathering signature than loess (Fig. S-8), and most experienced greenschist facies metamorphism (Han *et al.*, 2023).

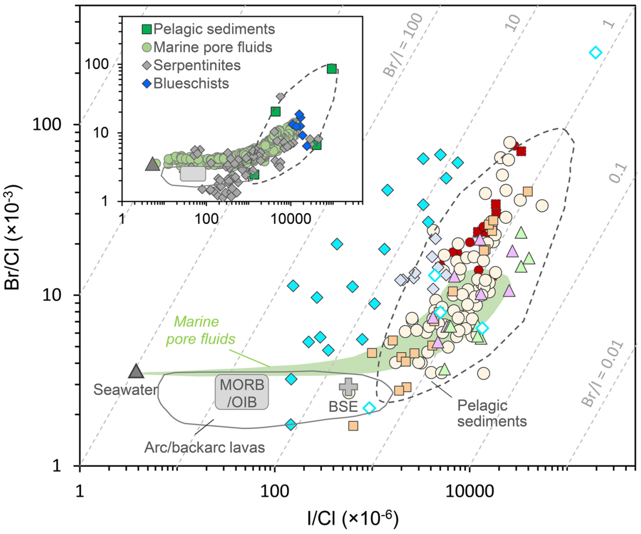

Figure 3 Br/Cl *versus* I/Cl ratios of loess (symbols as in Fig. 2; this study) and glacial diamictite composites (cyan diamonds; Han *et al.*, 2023). Note that (1) the leached loess residues are plotted as deep-red dashed symbols, and (2) five carbonate-rich and terrigenous sediment-rich glacial diamictites from Namibia have notably elevated I content and relatively low Br/I ratios and are shown with open diamonds (see Han *et al.*, 2023 for discussion). Halogen ratios of seawater (grey triangle), bulk silicate Earth (BSE, grey plus sign), mid-ocean ridge and ocean island basalts (MORB/OIB, grey rectangle, Kendrick *et al.*, 2017), arc/backarc lavas (grey outline, Kendrick *et al.*, 2020), pelagic sediments (grey dashed outline, John *et al.*, 2011), and marine pore fluids (green field, Fehn *et al.*, 2006; Muramatsu *et al.*, 2007) are plotted for comparison. Thin grey dashed lines are constant Br/I ratio contours, ranging from 0.01 to 10,000. The inset shows samples from the subduction zone setting: pelagic sediments, marine pore fluids, serpentinites (John *et al.*, 2011; Kendrick *et al.*, 2013), and blueschists (Pagé *et al.*, 2016).

Implications for Loess Provenance

Previous studies suggested that loess derives from rocks that have generally experienced moderate chemical weathering during multiple cycles of sedimentation (Gallet *et al.*, 1998; Sauzéat *et al.*, 2015). Based on the Li isotopic composition of loess, Sauzéat *et al.* (2015) estimated that the proportion of chemically weathered material at Earth's surface was 37^{+17}_{-10} %. However, because Li isotopes are not sensitive to the presence of organic matter, it remains unclear what proportion of material within loess is derived from pulverised unweathered crystalline bedrocks *versus* mature sediments that have extensively interacted with the biosphere. As Br and I are strongly enriched in organic-bearing sediments and their concentrations will be sensitive to the amount of such sediment in the loess provenance; we used a mixing model to calculate the proportions of the above sources in loess. In this calculation, the Br and I contents in loess are assumed to result from a mixture of (1) clastic sediments derived from glacially pulverised unweathered crystalline bedrocks, (2) an overlying halogen-rich sedimentary cover, and (3) inputs from other sources, such as precipitation (marine aerosols) and evaporite minerals (Fig. 4). Although the composition of the third end member is difficult to define and may vary between samples and locations, we assume that the first end member is well represented by the glacial diamictites (Han *et al.*, 2023), and the second by the Japanese soil samples (Yamasaki *et al.*, 2015). When projecting the geometric or arithmetic mean of Japanese soils (Fig. S-11) onto the mixing line for either Br or I, assuming no other inputs, the calculated mass proportions of the UCC crystalline bedrocks in loess are consistently >80–90 % (Fig. 4). This proportion would be even higher if other inputs were considered. Overall, this suggests that the sediments that have extensively interacted with the biosphere in the loess provenance is <10–20 %, which is somewhat lower than the sum proportion of chemically weathered components, 37^{+17}_{-10} %, at

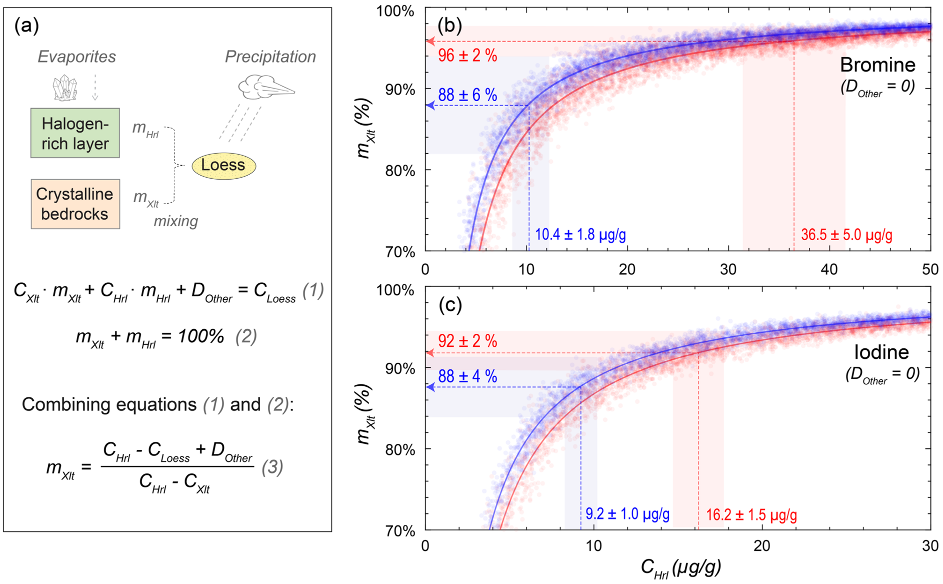

Figure 4 **(a)** Mixing model for the source of halogens in loess. In the equations, C_{Xlt}, C_{Hrl}, and C_{Loess} represent halogen concentrations of the UCC crystalline bedrocks, halogen-rich sedimentary layer, and loess, respectively; D_{Other} represents other potential inputs from precipitation and/or evaporites that could contribute significant halogens without substantially affecting the system's mass; m_{Xlt} and m_{Hrl} are assumed mass proportions of the UCC crystalline bedrocks and the sedimentary halogen-rich component in loess. **(b)** and **(c)** show the simulated relationship between m_{Xlt} and C_{Hrl} from Equation 3 in **(a)** when $D_{Other} = 0$, for mixing of Br and I, respectively. The red and blue curves are calculated using either the geometric (blue) or arithmetic (red) means of the loess samples and the adjacent pale red/blue circles represent related errors (modelled from Monte Carlo re-sampling; 10,000 times). The vertical dashed lines are geometric (in blue, 2 s.e.) and arithmetic (in red, 2 s.e.) means of Japanese soils. The calculated mass proportion of crystalline rocks in loess is shown as horizontal dashed lines (with 2σ uncertainties), which are obtained when projecting the geometric or arithmetic mean of Japanese soils (Fig. S-10) to the red or blue curves.

the continental surface as estimated by Sauzéat *et al.* (2015). Thus, it can be concluded that the primary source of loess material is the crystalline bedrocks of the UCC, which validates its use to infer the average composition of the present day UCC (Taylor *et al.*, 1983; Gallet *et al.*, 1998; Chauvel *et al.*, 2014).

Acknowledgements

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2442.

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References

Chauvel, C., Garçon, M., Bureau, S., Besnault, A., Jahn, B.-m., Ding, Z. (2014) Constraints from loess on the Hf–Nd isotopic composition of the upper continental crust. *Earth and Planetary Science Letters* 388, 48–58. https://doi.org/10.1016/j.epsl.2013.11.045

Fan, Y., Zhou, W., Hou, X., Kong, X., Chen, N., Burr, G.S. (2021) Indication of new climatic proxy by loess iodine variation. *Quaternary Science Reviews* 251, 106720. https://doi.org/10.1016/j.quascirev.2020.106720

Fehn, U., Lu, Z., Tomaru, H. (2006) Data report: ^{129}I/I ratios and halogen concentrations in pore water of Hydrate Ridge and their relevance for the origin of gas hydrates: A progress report. In: Tréhu, A.M., Bohrmann, G., Torres, M.E., Colwell, F.S. (Eds.) *Proceedings of the Ocean Drilling Program: Scientific Results Volume 204*. Texas A & M University, College Station, TX. 1–25. https://doi.org/10.2973/odp.proc.sr.204.107.2006

Feng, X., Steiner, Z., Redfern, S.A. (2021) Fluorine incorporation into calcite, aragonite and vaterite $CaCO_3$: Computational chemistry insights and geochemistry implications. *Geochimica et Cosmochimica Acta* 308, 384–392. https://doi.org/10.1016/j.gca.2021.05.029

Gallet, S., Jahn, B.-m., Lanoë, B.V.V., Dia, A., Rossello, E. (1998) Loess geochemistry and its implications for particle origin and composition of the upper continental crust. *Earth and Planetary Science Letters* 156, 157–172. https://doi.org/10.1016/S0012-821X(97)00218-5

Gao, S., Luo, T.C., Zhang, B.R., Zhang, H.F., Han, Y.W., Zhao, Z.D., Hu, Y.K. (1998) Chemical composition of the continental crust as revealed by studies in East China. *Geochimica et Cosmochimica Acta* 62, 1959–1975. http://dx.doi.org/10.1016/S0016-7037(98)00121-5

Gaschnig, R.M., Rudnick, R.L., McDonough, W.F., Kaufman, A.J., Valley, J.W., Hu, Z., Gao, S., Beck, M.L. (2016) Compositional of the upper continental crust through time, as constrained by ancient glacial diamictites. *Geochimica et Cosmochimica Acta* 186, 316–343. https://doi.org/10.1016/j.gca.2016.03.020

Han, P.-Y., Rudnick, R.L., He, T., Marks, M.A., Wang, S.-J., Gaschnig, R.M., Hu, Z.-C. (2023) Halogen (F, Cl, Br, and I) concentrations of the upper continental crust through time as recorded in ancient glacial diamictite composites. *Geochimica et Cosmochimica Acta* 341, 28–45. https://doi.org/10.1016/j.gca.2022.11.012

Hanley, J.J., Koga, K.T. (2018) Halogens in terrestrial and cosmic geochemical systems: abundances, geochemical behaviors, and analytical methods. In: Harlov, D., Aranovich, L. (Eds.) *The role of halogens in Terrestrial and Extraterrestrial Geochemical Processes*. Springer, Cham. 21–121. https://doi.org/10.1007/978-3-319-61667-4_2

He, T., Xie, J., Hu, Z., Liu, T., Zhang, W., Chen, H., Liu, Y., Zong, K., Li, M. (2018) A rapid acid digestion technique for the simultaneous determination of bromine and iodine in fifty-three Chinese soils and sediments by ICP-MS. *Geostandards and Geoanalytical Research* 42, 309–318. https://doi.org/10.1111/ggr.12212

John, T., Scambelluri, M., Frische, M., Barnes, J.D., Bach, W. (2011) Dehydration of subducting serpentinite: implications for halogen mobility in subduction zones and the deep halogen cycle. *Earth and Planetary Science Letters* 308, 65–76. https://doi.org/10.1016/j.epsl.2011.05.038

Kendrick, M.A. (2024) Halogen Cycling in the Solid Earth. *Annual Review of Earth and Planetary Sciences* 52. https://doi.org/10.1146/annurev-earth-031621-111700

Kendrick, M.A., Honda, M., Pettke, T., Scambelluri, M., Phillips, D., Giuliani, A. (2013) Subduction zone fluxes of halogens and noble gases in seafloor and forearc serpentinites. *Earth and Planetary Science Letters* 365, 86–96. https://doi.org/10.1016/j.epsl.2013.01.006

Kendrick, M., Hémond, C., Kamenetsky, V., Danyushevsky, L., Devey, C.W., Rodemann, T., Jackson, M., Perfit, M. (2017) Seawater cycled throughout Earth's mantle in partially serpentinized lithosphere. *Nature Geoscience* 10, 222–228. https://doi.org/10.1038/ngeo2902

Kendrick, M.A., Danyushevsky, L.V., Falloon, T.J., Woodhead, J.D., Arculus, R.J., Ireland, T. (2020) SW Pacific arc and backarc lavas and the role of slab-bend serpentinites in the global halogen cycle. *Earth and Planetary Science Letters* 530, 115921. https://doi.org/10.1016/j.epsl.2019.115921

Liu, Y., Wen, Q., Chen, Q. (1981) F/Cl ratio in Luochuan loess section, Shaanxi province—A geochemical index for paleoclimatic fluctuation. *Geochimica,* 388–391

Mayer, L.M., Schick, L.L., Allison, M.A., Ruttenberg, K.C., Bentley, S.J. (2007) Marine vs. terrigenous organic matter in Louisiana coastal sediments: The uses of bromine: organic carbon ratios. *Marine Chemistry* 107, 244–254. https://doi.org/10.1016/j.marchem.2007.07.007

Muramatsu, Y., Wedepohl, K.H. (1998) The distribution of iodine in the earth's crust. *Chemical Geology* 147, 201–216. https://doi.org/10.1016/S0009-2541(98)00013-8

Muramatsu, Y., Doi, T., Tomaru, H., Fehn, U., Takeuchi, R., Matsumoto, R. (2007) Halogen concentrations in pore waters and sediments of the Nankai Trough, Japan: Implications for the origin of gas hydrates. *Applied Geochemistry* 22, 534–556. https://doi.org/10.1016/j.apgeochem.2006.12.015

Pagé, L., Hattori, K., de Hoog, J.C., Okay, A.I. (2016) Halogen (F, Cl, Br, I) behaviour in subducting slabs: A study of lawsonite blueschists in western Turkey. *Earth and Planetary Science Letters* 442, 133–142. https://doi.org/10.1016/j.epsl.2016.02.054

Pye, K. (1995) The nature, origin and accumulation of loess. *Quaternary Science Reviews* 14, 653–667. https://doi.org/10.1016/0277-3791(95)00047-X

Ramos, A., Ohde, S., Hossain, M., Ozaki, H., Sirirattanachai, S., Apurado, J. (2005) Determination of fluorine in coral skeletons by instrumental neutron activation analysis. *Journal of radioanalytical and nuclear chemistry* 266, 19–29. https://doi.org/10.1007/s10967-005-0863-x

Rude, P.D., Aller, R.C. (1991) Fluorine mobility during early diagenesis of carbonate sediment: An indicator of mineral transformations. *Geochimica et Cosmochimica Acta* 55, 2491–2509. https://doi.org/10.1016/0016-7037(91)90368-F

Rudnick, R.L., Gao, S. (2003) Composition of the Continental Crust. *Treatise on Geochemistry,* 1–64. https://doi.org/10.1016/B0-08-043751-6/03016-4

Sauzéat, L., Rudnick, R.L., Chauvel, C., Garçon, M., Tang, M. (2015) New perspectives on the Li isotopic composition of the upper continental crust and its weathering signature. *Earth and Planetary Science Letters* 428, 181–192. https://doi.org/10.1016/j.epsl.2015.07.032

Shaw, D., Reilly, G., Muysson, J., Pattenden, G., Campbell, F. (1967) An Estimate of the Composition of the Canadian Precambrian shield. *Canadian Journal of Earth Sciences* 4, 829–853. https://doi.org/10.1139/e67-058

Taylor, S.R., Mclennan, S.M., McCulloch, M.T. (1983) Geochemistry of loess, continental crustal composition and crustal model ages. *Geochimica et Cosmochimica Acta* 47, 1897–1905. https://doi.org/10.1016/0016-7037(83)90206-5

Wedepohl, K.H. (1995) The composition of the continental crust. *Geochimica et Cosmochimica Acta* 59, 1217–1232. https://doi.org/10.1016/0016-7037(95)00038-2

Worden, R.H. (2018) Halogen Elements in Sedimentary Systems and Their Evolution During Diagenesis. In: Harlov, D., Aranovich, L. (Eds.) *The Role of Halogens in Terrestrial and Extraterrestrial Geochemical Processes*. Springer, Cham. 185–260. https://doi.org/10.1007/978-3-319-61667-4_4

Yamasaki, S.-i., Takeda, A., Watanabe, T., Tagami, K., Uchida, S., Takata, H., Maejima, Y., Kihou, N., Tsuchiya, N. (2015) Bromine and iodine in Japanese soils determined with polarizing energy dispersive X-ray fluorescence spectrometry. *Soil Science and Plant Nutrition* 61, 751–760. https://doi.org/10.1080/00380768.2015.1054773