



NOBLE GAS AND HALOGEN HETEROGENEITY IN THE SUBCONTINENTAL LITHOSPHERIC MANTLE

Hirochika SUMINO¹, Masahiro KOBAYASHI², Ray BURGESS³ and Chris BALLENTINE⁴

¹University of Tokyo, Tokyo 153-0041, Japan; sumino@igcl.c.u-tokyo.ac.jp

²Tokyo Metropolitan Industrial Technology Research Institute, Tokyo 135-0064, Japan

³University of Manchester, Manchester M13 9PL, UK

⁴University of Oxford, Oxford OX1 3AN, UK

Introduction

Volatile recycling back to the Earth's mantle at subduction zones has a significant, yet poorly constrained impact to the volatile budget in the mantle. Halogen and noble gas systematics are powerful tracers of volatile recycling. The presence of noble gases and halogens with seawater and sedimentary pore-fluid signatures in exhumed mantle wedge peridotites from the Sanbagawa-metamorphic belt, southwest Japan (Sumino *et al.*, 2010), and in forearc serpentinites (Kendrick *et al.*, 2013) along with seawater-like heavy noble gases (Ar, Kr, and Xe) in the convecting mantle (Holland and Ballentine, 2006) strongly suggest the subduction of sedimentary-pore-fluid-like noble gases and halogens. In order to better constrain how such subduction fluids may modify the halogen composition of subcontinental lithospheric mantle, we have been investigating halogens and noble gases in mantle-derived xenoliths from volcanic front and back-arc regions of subduction zones, and intraplate continental settings.

Samples and methods

The samples were mantle peridotite xenoliths containing H₂O-rich fluid inclusions collected at volcanic fronts from two contrasting subduction zones (the Avacha volcano of Kamchatka arc and the Pinatubo volcano of Luzon arcs) and orogenic peridotites from a peridotite massif (the Horoman massif, Hokkaido, Japan) which represents an exhumed portion of the mantle wedge (Kobayashi *et al.*, 2017). The back-arc region samples were from Southern Patagonia, where two metasomatic noble gas components have been observed previously: a degassed SCLM component with a radiogenic/nucleogenic composition; and a MORB-like component, the latter may result from the presence of a slab-window (Jalowitzki *et al.*, 2016). The samples from intraplate settings were collected from Eifel (Central Europa), San Carlos, and Kilbourne Hole (North America) (Kobayashi *et al.*, 2019).

Some of the samples were neutron-irradiated in a nuclear reactor to convert halogens to noble gas isotopes (³⁸Ar_{Cl}, ⁸⁰Kr_{Br} and ¹²⁸Xe_I). Noble gases in the unirradiated and irradiated samples were extracted selectively from the fluid inclusions using a combination of in vacuo crushing. The evolved noble gases were analysed using mass spectrometry at the University of Tokyo and University of Manchester.

Results and Discussion

In addition to a MORB-like noble gas and halogen component observed in most of the samples, three other distinct components were identified: (A) a marine-pore-fluid-like component with atmospheric noble gases and high Br/Cl and I/Cl ratios similar to mantle wedge peridotites [1], (B) a Cl-enriched component relative to MORB, similar to bulk altered oceanic crust (Chavrit *et al.*, 2016); and (C) a component enriched in Br and moderately in I compared to MORB, which resembles to fluid components in altered oceanic crust and diamonds (Burgess *et al.*, 2009; Chavrit *et al.*, 2016; Broadley *et al.*, 2018).

The component (A) is typically observed in the volcanic front samples containing abundant H₂O-rich fluid inclusions. This suggests that marine pore fluids in deep-sea sediments are carried by serpentine and supplied to the mantle wedge, preserving their original halogen and noble gas compositions. However, the measured Cl/H₂O and ³⁶Ar/H₂O in the peridotites are higher than those in sedimentary pore fluids and serpentine in oceanic plates (Kendrick *et al.*, 2013). The halogen/noble gas/H₂O systematics are interpreted within a model where water is incorporated into serpentine in a closed system formed along fracture zones developed at the outer rise, where oceanic plates bend prior to entering subduction zones, preserving Cl/H₂O and ³⁶Ar/H₂O



values of sedimentary pore fluids. Dehydration-hydration process within the oceanic lithospheric mantle maintains the closed system until the final stage of serpentine dehydration. The sedimentary pore fluid-like halogen and noble gas signatures in fluids released at the final stage of serpentine dehydration are preserved due to highly channelized flow (Kobayashi *et al.*, 2017).

The samples involving the component (B) have higher Cl concentration and trace elements ratios, whereas the samples involving the component (C) have relatively low Cl concentration and low ratios of highly incompatible elements relative to heavy rare earth elements. Considering that these two components are observed in some back-arc samples having radiogenic/nucleogenic noble gases (Jalowizki *et al.*, 2016), they could be remnants of metasomatic agents derived from subducted altered oceanic crust, or could result from secondary processes of volatile loss during partial melting and secondary phase formation during interaction with melts (Kobayashi *et al.*, 2019).

The common primary MORB-like halogen ratios in mantle xenoliths from different parts of the globe indicate that the mantle itself must have a relatively uniform composition over a wide scale. The mantle has maintained its halogen composition over billion year timescales without being affected by I-rich halogens being transported into the mantle. Mass balance calculations suggest that, in order to maintain the I/Cl ratio of the convecting mantle over 2 Gyr, the I/Cl ratio of the subducted halogens must be no more than several times higher than the present-day mantle value (Kobayashi *et al.*, 2019).

References

- Burgess, R., Cartigny, P., Harrison, D., Hobson, E., Harris, J., 2009. Volatile composition of microinclusions in diamonds from the Panda kimberlite, Canada: Implications for chemical and isotopic heterogeneity in the mantle. *Geochim. Cosmochim. Acta* 73, 1779-1794.
- Broadley, M.W., Kagi, H., Burgess, R., Zedgenizov, D., Mikhail, S., Almayrac, M., Ragozin, A., Pomazansky, B., Sumino, H., 2018. Plume-lithosphere interaction, and the formation of fibrous diamonds. *Geochemical Perspectives Letters* 8, 26-30.
- Chavrit, D., Burgess, R., Sumino, H., Teagle, D.A.H., Droop, G., Shimizu, A., Ballentine, C.J., 2016. The contribution of hydrothermally altered ocean crust to the mantle halogen and noble gas cycles. *Geochim. Cosmochim. Acta* 183, 106-124.
- Holland, G., Ballentine, C.J., 2006. Seawater subduction controls the heavy noble gas composition of the mantle. *Nature* 441, 186-191.
- Jalowitzki, T., Sumino, H., Conceição, R.V., Orihashi, Y., Nagao, K., Bertotto, G.W., Balbinot, E., Schilling, M.E., Gervasoni, F., 2016. Noble gas composition of subcontinental lithospheric mantle: An extensively degassed reservoir beneath Southern Patagonia. *Earth Planet. Sci. Lett.* 450, 263-273.
- 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 Planet. Sci. Lett.* 365, 86-96.
- Kobayashi, M., Sumino, H., Nagao, K., Ishimaru, S., Arai, S., Yoshikawa, M., Kawamoto, T., Kumagai, Y., Kobayashi, T., Burgess, R., Ballentine, C.J., 2017. Slab-derived halogens and noble gases illuminate closed system processes controlling volatile element transport into the mantle wedge. *Earth Planet. Sci. Lett.* 457, 106-116.
- Kobayashi, M., Sumino, H., Burgess, R., Nakai, S.i., Iizuka, T., Nagao, J., Kagi, H., Nakamura, M., Takahashi, E., Kogiso, T., Ballentine, C.J., 2019. Halogen Heterogeneity in the Lithosphere and Evolution of Mantle Halogen Abundances Inferred From Intraplate Mantle Xenoliths. *Geochemistry, Geophysics, Geosystems* 20, 952-973.
- Sumino, H., Burgess, R., Mizukami, T., Wallis, S.R., Holland, G., Ballentine, C.J., 2010. Seawater-derived noble gases and halogens preserved in exhumed mantle wedge peridotite. *Earth Planet. Sci. Lett.* 294, 163-172.