

Hot CD-MUSIC

M. L. MACHESKY^{1*}, D. J. WESOŁOWSKI², M. K. RIDLEY³, M. PŘEDOTA⁴, Z. ZHANG⁵, P. A. FENTER⁵
AND J. D. KUBICKI⁶

¹Univ. of Illinois, Illinois State Water Survey, Champaign IL, USA, (*correspondence: machesky@illinois.edu)

²Oak Ridge National Laboratory, Oak Ridge, TN, USA (dqw@ornl.gov)

³Texas Tech Univ., Dept. of Geosciences, Lubbock, TX, USA, (moira.ridley@ttu.edu)

⁴Univ. South Bohemia, České Budějovice, Czech Republic (predota@prf.jcu.cz)

⁵Argonne National Laboratory, Argonne, IL 60439, USA (zhazhang@anl.gov, Fenter@anl.gov)

⁶The Pennsylvania State Univ., University Park, PA 16802, USA, (jdk7@psu.edu)

Among the many seminal contributions of Professor van Riemsdijk is the CD-MUSIC model, which was developed in collaboration with Professor Hiemstra, and has remained the state-of-the-art Surface Complexation Model since its publication in 1996[1]. Also in the mid-1990's our group began investigating ion adsorption phenomena (primarily cations) over a wide range of temperatures extending into the hydrothermal regime (10-250°C), mostly on rutile, but also on several other metal oxides[2]. More recently, we have also complimented these macroscopic data with a variety of molecular-level information, including X-ray synchrotron experiments, and static DFT as well as classical molecular dynamics (MD) simulations. CD-MUSIC has proven to be a sturdy framework within which we have been able to coherently interpret this assortment of data[3,4].

This contribution will summarize our efforts to rationalize adsorption data for rutile to 250°C within the CD-MUSIC model framework with particular focus on Sr²⁺ and Zn²⁺. Our classical MD simulations suggest that the enhanced adsorption observed macroscopically as temperature increases is due to adsorbed cations moving closer to the surface and shedding more bulk hydration water in the process. CD-MUSIC can mimic this behavior although the agreement is not perfect, suggesting extensions to CD-MUSIC may be warranted.

[1] Hiemstra & van Riemsdijk (1996) *JCIS* **179**, 488-508.

[2] Machesky *et al.* (2006) *Interface Sci. Tech.* **11**, 324-358.

[3] Ridley *et al.* (2009) *GCA* **73**, 1841-1856.

[4] Ridely *et al.* (2012) *GCA* **95**, 227-240.

Geochemical variations of basalts from petit-spot volcanoes in the northwestern Pacific

S. MACHIDA^{1,2*}, N. HIRANO³, Y. KATO², A. TAMURA⁴
AND S. ARAI⁴

¹ School Creative Sci. Engineer., Waseda Univ., Tokyo 169-8555, Japan (*correspondence: m-shikit@aoni.waseda.jp)

² School of Engineer., Univ. of Tokyo, Japan

³ Center NE Asian Studies, Tohoku Univ., Japan

⁴ Grad. School of Sci., Kanazawa Univ., Japan

Petit-spot, new type young volcanoes discovered on the old Pacific plate, originate from melting in the uppermost mantle asthenosphere, and that the magma exudes where the plate flexes and fractures before subducting [1]. Our recent studies defined that alkaline basalt lavas from petit-spot show (1) high concentrations of incompatible trace elements indicating extreme enrichment in highly incompatible elements (e.g., Rb, Ba, U, Th, and Nb) and REE, and depletion in heavy REE [1], and (2) extreme EM-1-like, Sr, Nd, and Pb isotopic compositions [2]. These results indicate that melting of small-scale recycled plate material produces petit-spot magma [2]. Thus, detailed geochemical investigation for these petit-spot volcanoes will provide key constraints on our understanding of the nature of heterogeneity of the northwestern Pacific upper mantle.

Basalts were collected from twelve petit-spot volcanoes at a site in the Japan Trench (Site A), a site approximately 600 km ESE of the Site A (Site B), and a site approximately 200 km S of the Site A (Site C). Five distinct compositional groups are identified on the basis of their major and trace element compositions. The Group 1 basalts (G1), from the Sites A and C, are enriched in LILEs and LREEs. Then, they show negative U, Th, Nb, and Ta anomalies. The Group 2 basalts (G2) from the Site A show negative U, Th, Nb, Ta, Zr, and Hf anomalies, and higher alkali contents than G1. However, on the basis of other major element characteristics, G2 are further subdivided into three groups. G2-2 have lower SiO₂ and higher FeO*/MgO than G2-1 (and G1). G2-3 show a similar major element signature to G2-2, except for lower CaO. The Group 3 basalts, obtained from Site B, show lower SiO₂ and higher FeO*/MgO than G2-2, and negative Zr and Hf anomalies. Variation of Ba/Nb of basalts from all groups correlates to Sr and Nd isotopic compositions. These observations suggest that the source heterogeneity for petit-spot magma is regulated by degree of contributions of LILEs and LREEs-enriched material.

[1] N. Hirano *et al.* (2006) *Science*, **313**, 1426-1428. [2] S. Machida *et al.* (2009) *GCA*, **73**, 3028-3037.