

## Mantle wedge metasomatism recorded in LREE-depleted calcic amphibole in the Pinatubo harzburgite xenoliths

M. YOSHIKAWA<sup>\*1</sup>, T. KAWAMOTO<sup>1</sup>, Y. KUMAGAI<sup>1</sup>,  
S. ARAI<sup>2</sup>, A. TAMURA<sup>2</sup>, T. KOBAYASHI<sup>3</sup>  
AND M. OKUNO<sup>4</sup>

<sup>1</sup> Kyoto Univ., Beppu, 874-0903, Japan (\*correspondence: masako@bep.vgs.kyoto-u.ac.jp)

<sup>2</sup> Kanazawa Univ., Kanazawa 920-1192, Japan

<sup>3</sup> Kagoshima Univ., Kagoshima 890-0065, Japan

<sup>4</sup> Fukuoka Univ., Fukuoka 814-0180, Japan

Calcic amphibole-bearing spinel harzburgites from the Pinatubo 1991 dacite are characterized by residual mantle mineral chemistry and abundant fluid inclusions of saline solutions and magnesite in mantle minerals. Some xenoliths have zoned selvages composed of amphibole, phlogopite, plagioclase and orthopyroxene. The peridotite xenoliths show more or less metasomatized textures; fine-grained orthopyroxene-rich parts with amphibole, olivine, spinel, and phlogopite, replacing primary olivines. We determined trace element compositions of amphiboles of the least metasomatized harzburgite using LA-ICP-MS.

Chondrite-normalized trace element patterns of the amphiboles show depletion in LREE with various degrees of negative Ti and positive Sr anomalies, in contrast to LREE enriched amphiboles with negative anomalies of HFSE, Eu and Sr from the selvages. This suggests that the harzburgites were metasomatized before entrainment in the host dacite. Amphiboles inside the harzburgite xenolith show continuous chemistry from magnesiohornblende to tremolite. These amphiboles can be classified into primary and secondary ones in paragenesis and chemical composition. The secondary amphiboles are contained in the fine-grained orthopyroxene rich parts and show relatively low TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, and high SiO<sub>2</sub> and MgO contents. Their trace element patterns are similar to those of primary amphiboles but with lower concentrations. These LREE-depleted amphiboles have been observed in the subcontinental lithospheric mantle peridotites metasomatized by subduction-related hydrous fluids, because hydrous fluids do not carry large amounts of REE [1, 2]. The compositional features of the amphiboles suggest that the primary amphiboles were formed through a reaction between pyroxene and subduction-related SiO<sub>2</sub>-rich aqueous fluids and the secondary amphiboles were formed from more diluted fluids at lower temperature conditions.

[1] Vannucci *et al.* (1995) *GCA* **59**, 1763-1771. [2] Downes (2001) *J. Petrol.* **42**, 233-250.

## Apparent inverse carbon isotope effects during the anaerobic oxidation of methane

MARCOS YOSHINAGA<sup>1</sup>, GUNTER WEGENER<sup>1,2\*</sup>,  
THOMAS<sup>2</sup> HOLLER, TOBIAS GOLDHAMMER<sup>2</sup>,  
BENJAMIN BRUNNER<sup>2</sup>, JOHN POHLMAN<sup>3</sup>,  
MARCEL KUYPERS<sup>2</sup>, KAI-UWE HINRICH<sup>1</sup>  
AND MARCUS ELVERT<sup>1</sup>

<sup>1</sup>Marum, Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany (\*presenting author)

<sup>2</sup>Max Planck Institute for Marine Microbiology, Bremen, Germany

<sup>3</sup>U.S. Geological Survey, Woods Hole Coastal and Marine Science Center, Massachusetts, USA

Large amounts of methane are produced in marine subsurface sediments. Their emission to the hydrosphere is suppressed by microbial consortia, which perform the sulfate-dependent anaerobic oxidation of methane (AOM) in distinct sulfate-methane transition zones (SMTZ). According to conventional isotope systematics, the biological consumption should result in <sup>13</sup>C-enriched residual methane. Instead, within the SMTZs methane is often depleted in <sup>13</sup>C, a pattern frequently interpreted as evidence of concomitant methane production.

Here we tested if AOM alone can yield <sup>13</sup>C-depleted methane. We incubated sediment-free AOM-cultures devoid of background methanogenesis at low sulfate concentrations. As a result of decreasing sulfate availability (<0.5 mM), the system switched from <sup>13</sup>C-enrichment towards <sup>13</sup>C-depletion in the methane pool. We explain this apparent inverse carbon isotope effect by AOM-mediated equilibrium isotope exchange, which predominates during sulfate-limited AOM. Our results are representative of SMTZs, where generally low sulfate concentrations prevail. Evidence that <sup>13</sup>C-depleted methane can form by a non-methanogenic process expands our current understanding of the methane biogeochemistry in marine sediments. Microbially mediated equilibrium isotope exchange might be common in marine subsurface habitats, which are generally characterized by limited substrate availability combined with low energy yields.