



Generation of high reactive fluids by rapid clinopyroxene-seawater interaction: An experimental study at 425 °C, 40 and 100 MPa

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Submarine hydrothermalism with extensive alteration of oceanic crust is a major process governing energy and mass fluxes from Earth's interior into the oceans. Recent investigations revealed high element fluxes discharging in particular from the generally brittle deformed slow and ultra-slow spreading Mid-Atlantic Ridge (MAR) [1, 2, 3]. This suggests that seawater access to unaltered rocks along juvenile fault systems of the MAR may create hydrothermalism with high fluid and high element fluxes. For example hydrothermal venting at 5° S MAR [4, 5] intensified after a volcano-tectonic event in 2002 [5] and vent fluids constantly emanate here in ~3000 m bsl (~30 MPa) at extreme temperatures above 407 °C [2, 5, 6] and contain high concentrations of transition metals and rare earth elements (REE) [2]. However, geochemical models on mass transfer between oceanic lithosphere and ocean are based upon time integrated mass balance between vent fluid and host rock geochemistry [e.g., 7, 8, 9]. But, none of these models provide estimates for early-stage high-temperature hydrothermalism with unaltered host-rocks as it is evident from the 5°S MAR hydrothermal system.

In order to unravel the temporal evolution on element mass transfer between seawater fluid and ocean lithosphere during high-temperature hydrothermalism we started a systematic time-resolved experimental study on seawater-rock interaction processes at variable water-to-rock mass ratios (w/r-ratios). Mixtures of 125-500 μm-sized clinopyroxene (Cpx) and plagioclase (Plag) grains prepared from unaltered gabbro (Atlantis Massif, 30°N MAR, IODP expedition 305, Site U1309D, core sample R211, 1020 m bsf) reacted with two fluid types of similar chlorinity, natural bottom seawater or synthetic 3.2 wt.% NaCl(aq), at 425 °C, 400 and 1000 bar and at w/r ratios from 0.5 to 10 and run durations from 3 to 720 hours. Solid products were analyzed by SEM and XRD, and fluid products were analyzed by ICP-MS and ICP-OES.

In all experiments significant amounts (~10-20 rel. %) of secondary mineral phases, i.e. talc, the serpentine-group minerals lizardite, antigorite, and chrysotile, and minor abundances of pyrrhotite and pentlandite were formed primarily on Cpx even after short run durations of 3 hours. Our results show that intense leaching of Ca, REEs, transition and trace metals only occurred with Cpx and only in the seawater experiments. Leaching was caused by rapid precipitation of the initial seawater Mg (1400 ppm) on Cpx, which generated HCl(aq) with pH (25 °C) < 2 prior to significant leaching.

Because element exchange reactions between seawater and the other widespread abundant mineral olivine in the oceanic lithosphere are very sluggish at elevated pressure and temperature conditions [10], we conclude that in particular seawater interactions with un-leached pyroxenes creates high element fluxes during early-stage, high temperature MOR hydrothermalism, as it is evident from MAR 5° S fluids. This kind of hydrothermalism is expected to be not uncommon in particular at the slow-spreading MAR [9], and the high element fluxes here, most probably caused by seawater-pyroxene interactions, should be taken into account when modelling global chemical fluxes of MOR hydrothermalism.

References:

- [1] German C. R., Thurnherr A. M., Knoery J., Charlou J.-L., Jean-Baptiste P., and Edmonds H. N. (2010) *Deep Sea Res.* 157, 518-527.
- [2] Schmidt K., Garbe-Schönberg D., Bau M., and Koschinsky A. (2010) *Geochim. Cosmochim. Acta* 74, 4058-4077.
- [3] Saito M. A., Noble A. E., Tagliabue A., Goepfert T. G., Lamborg C. H., and Jenkins W. J. (2013) *Nat. Geosci.* 5, 775-779.
- [4] German C. R., Bennett S. A., Connelly D. P., Evans A. J., Murton B. J., Parson L. M., Prien R. D., Ramirez-Llodra E., Jakuba M., Shank T. M., Yoerger D. R., Baker E. T., Walker S. L., and Nakamura K. (2008) *Earth. Planet. Sci. Lett.* 273, 332-344.
- [5] Haase K. M., Petersen S., Koschinsky A., and M64/1, M68/1 *Scient. Parties* (2007) *Geochem. Geophys. Geosyst.* 8, Q11002, doi: 10.1029/2006GC001509.

- [6] Koschinsky A., Garbe-Schönberg D., Sander S., Schmidt K., Gennerich H. H., and Strauss H. (2008) *Geology* 36, 615–618.
- [7] Elderfield H. and Schultz A. (1996) *Annu. Rev. Earth Planet. Sci.*, 24, 191-224.
- [8] German C. R., Thurnherr A. M., Knoery J., Charlou J.-L., Jean-Baptiste P., and Edmonds H. N. (2010) *Deep Sea Res.* 157, 518-527.
- [9] Coogan L. A. and Dosso S. (2012) *Earth. Planet. Sci. Lett.* 323-324, 92-101.
- [10] Allen D. E. and Seyfried [Jr.] W. E. (2003) *Geochim. Cosmochim. Acta* 67, 1531-1542.