

## Thermal-flow structure and fluid processes in subduction zones: implications for hydrothermal vein-type ore deposits

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Fluid processes in subduction zones are key to understanding the Earth's fundamental features distinct from other solar planets, with respect to geological, geochemical and geophysical aspects; e.g., active tectonics including earthquake, hydrothermal activity, ore formation and arc magmatism, as well as longer-term evolution of the continental crust and orogeny, all of which are thought to be assisted or driven by presence of fluids. This subduction zone system with fluids involves the following schemes:

- (1) thermal and flow structure associated with mantle convection and slab subduction,
- (2) phase relation and chemical reaction, including generation of fluids,
- (3) fluid migration and its interaction with the solid convective flow.

First, we discuss these schemes mainly based on numerical simulation, in which importance of non-linear feedback via water-rock interaction has been found (Horiuchi, 2012). Second, we compare the model predictions with the observations, such as geochemistry of volcanic rocks and hydrothermal fluids, which highlights the trace element and isotopic characteristics of slab-derived fluids (e.g., Nakamura et al., 2008), particularly lead geochemistry, as well as those of volcanic rocks and the arc crust.

Then, hydrothermal activity, including vein-type ore formation, is discussed in this framework of the subduction zone system. Unlike conventional studies based on isotopic compositions of hydrogen and oxygen, this study tracks directly ore-forming metals in terms of their abundances and isotopic compositions. New geochemical data on ore deposits from the Toyoha mine (Hokkaido) and the surrounding country rocks includes trace element abundances and Nd-Pb-He isotopic compositions, many of which are the first-ever data (Hieda, 2013). The results suggest that the ore deposits exhibit appreciable enrichment in "slab-fluid component" (e.g., more radiogenic Pb isotopic ratios) compared to the nearby Muine volcanic rocks contemporary with the ore deposits, together with a mantle He component. Based on the elemental partitioning and mass balance calculations, two plausible models have been proposed to explain the isotopic compositions and the total Pb reserve (5.3 x 10<sup>5</sup> ton): one assumes direct contribution of slab-fluid (Nakamura and Iwamori, 2009), whereas another involves the Muine magma-derived lead as well as slab-fluid contribution. Both models may explain the characteristics of the Toyoha ore deposits, suggesting potential importance of deep circulation with slab-derived fluid as a source of hydrothermal vein-type deposits.

Keywords: subduction zone, fluid, ore

## Boron content and isotopic composition of vent fluids from seafloor arc-backarc hydrothermal systems

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Boron content and isotopic composition of vent fluids collected from seafloor arc-backarc hydrothermal systems in the western Pacific are determined in order to investigate boron behavior during water-rock reaction at high temperature. In sediment-starved hydrothermal systems (Manus Basin, Suiyo Seamount, and Mariana Trough), the boron content and isotopic composition of vent fluids are dependent on type of host rock. The vent fluids from MORB-like basalt-hosted Vienna Woods in the Manus Basin showed low boron content and high  $\delta^{11}\text{B}$  value, while dacite-hosted PACMANUS and the Suiyo Seamount showed high boron contents and low  $\delta^{11}\text{B}$  values. The Alice Springs and Forecast Vent field in the Mariana Trough showed values intermediate between them, reflecting reaction of seawater and basalt influenced by slab material. In phase separated hydrothermal systems (North Fiji Basin), boron content and isotopic composition of vent fluids were similar to those in the Vienna Woods. Considering little fractionation of boron and boron isotope during phase separation demonstrated by the previous experimental studies, it is suggested that the host rock in the North Fiji Basin is MORB-like basalt. In sediment-hosted hydrothermal system (Okinawa Trough), the reaction with boron-enriched sediment following seawater-rock reaction resulted in significantly high boron contents and low  $\delta^{11}\text{B}$  values of vent fluids. The water-sediment ratio was estimated to be  $\sim 2$ .

Keywords: seafloor hydrothermal system, boron isotope

## Magmatic fluid leading to epithermal gold deposits; probability of porphyry copper deposits in Japan

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Epithermal gold deposits (<1km depth) have spatial and temporal links to porphyry style deposits (2-5km depth) associated with hydrous magmatism. The magmatic fluids containing significant vapor after physical phase separation within porphyry style deposits could effectively transport gold to epithermal environments, which has theoretically been inferred by recent thermodynamic data.

However, the ore-forming fluid passes connecting porphyry to epithermal environments and gold contributor into epithermal environments is still in the debate. Moreover, there are two main types of epithermal gold deposit composing high- and low-sulfidation styles which are characterized by the presence of enargite as well as luzonite, and adularia and calcite, respectively; this diversification have not substantially been proven yet.

In this study, epithermal gold deposits such as Hishikari deposit (low-sulfidation) and Kasuga and Akaishi deposit (high-sulfidation) in Kagoshima Prefecture, in addition to Furikusa sericite deposit in Aichi Prefecture were studied using Laser Ablation ICPMS (LA-ICPMS) analysis based on microthermometry. The results demonstrate major and minor elements in fluid inclusion, ore-forming fluids which were trapped in hydrothermal gangue minerals such as quartz, paying special attention to Au and S concentrations. I discuss that spatial and chemical affinities between epithermal gold deposits and porphyry style deposits with a focus on the formation depth of porphyry style deposits.

Here I report magmatic epithermal fluids readily transported S, Cu, Au, As, and Sb which lead to high and low-sulfidation epithermal gold deposits. For example, the concentration of major elements in the fluids for mineralized epithermal gold deposits has ranges of 1.5-6.5 ug/g Au, several tens ug/g As and Cu, several hundred ug/g Sb. Especially, the magmatic vapor in barren hydrothermal system of Furikusa deposit has similar chemical compositions to a hypothetical process described by an ascending magmatic vapor to a shallower high-sulfidation gold deposit. This represents gold transported through the barren alteration zone containing sericite-pyrite-quartz, closely resembles to the later stage of QSP veins in typical porphyry copper deposits.

For sulfur contents, ore-forming fluid for high-sulfidation gold deposit shows several thousand ug/g, while several hundred for low-sulfidation. The difference in sulfur content directly reflects the difference in sulfur fugacity between both styles of epithermal gold deposits. Compared with the vapor phase in porphyry copper deposits, the epithermal fluids show similar gold concentrations, two to three orders of magnitude lower concentration of copper, and very low sulfur concentration in the low-sulfidation style.

The following formation process can be assumed; 1) boiling fluid derived from the magma associated with porphyry style deposit, 2) separated vapor phase, enriched in S and Au, rises to shallow environment and forms sulfide and hydrothermal minerals corresponding to QSP-vein (Quartz-Sericite-Pyrite vein) in a porphyry copper deposit, suggesting that gold is transported as thio-complexes. During the process of 1) and 2), copper and sulfur in the fluid were consumed and decreased. In other words, it suggests that high-sulfidation gold deposit was formed at distance relatively close to the magma, whereas low-sulfidation style was far from the magma. This probably indicates that porphyry style deposit can be present at deeper level from the low-sulfidation style gold deposits relative to a depth from high-sulfidation style.

Therefore, I propose a paradigm as "discrimination between low- and high-sulfidation style gold deposits can be attributed to the difference in formation depth of porphyry style deposits". This findings may have vital implications that might give rise to further potential for undiscovered porphyry style deposits underneath (>2-3km depth) the epithermal gold deposits in Japan.

Keywords: Epithermal gold deposit, Porphyry copper deposit, Magmatic fluid, LA-ICPMS, Fluid inclusion

## Lithium origin in playa at Nevada, USA: constrains by lithium isotope ratio

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Highly concentrated lithium resources are often formed in salt crusts and playas by repetition of water evaporation and inspissation. Lithium-rich brine in playas has been the major raw material for lithium production worldwide. Recently, lithium isotopic ratio has been known as a new tool for understanding water-rock interaction. To estimate lithium origin in playas, we conducted two kinds of leaching experiment to evaluate the change of lithium isotopic ratios via leaching process, and determined isotopic ratios and contents of lithium and strontium as well as trace element contents, of various lacustrine and evaporite deposit samples collected from several playas in Nevada, USA.

The lithium isotopic values of the samples from the playas were much lower than those of river and ground waters in the world, and close those of volcanic rocks. The lithium isotopic results suggested that lithium concentrated in playas had been supplied mainly by water-rock interaction at high temperature by local hydrothermal activities, not directly by surface weathering processes at low temperature.

This is consistent with the positive correlation between temperature and lithium isotopic ratio during water-rock interaction. This study is the first to report lithium isotopic composition at playas, demonstrating that the lithium isotopic ratio has a large potential to trace the origin of lithium and the lithium accumulation processes in playas.

Keywords: lithium isotope, Playa, evaporite, lacustrine deposit, lithium resource, Nevada

## Possibility of man-made ore deposit originated from acid hot spring

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Tamagawa hot spring in Akita Prefecture is one of representative acid hot spring in Japan. Main hot spring is Obuki (sometimes Obuke in local pronunciation) of which pH is 1.2 and 9000L/min discharge. Tamagawa hot spring contains much amount of rare metal and rare earth elements, and Tamagawa hot water is neutralized in the plant which is constructed in the downstream of accommodation facilities.

Tamagawa hot water flows down to Shibukuro-gawa River, and then confluent with Tama-gawa River.

Two dams, Tamagawa Dam (Hosenko Lake) and Yoroihata Dam (Shusen-ko Lake), were constructed in Tama-gawa River, and Tama-gawa River flows down to Tazawa-ko Lake and surrounding area.

Strong acid water and metal elements in the river water were prevented to flow to downstream by Tamagawa Dam and Yoroihata Dam. In other words, sediments by the Dam could contain certain amount of metal elements as a man-made ore deposits. In this presentation, I will show precipitation behaviors of rare and rare earth elements and describe a possibility of rare metal resources.

Ogawa et al., 2012, The role of hydrous ferric oxide precipitation in the fractionation of arsenic, gallium, and indium during the neutralization of acidic hot spring water by river water in the Tama River watershed, Japan. [Geochimica Cosmochimica Acta, 86, (2012), 367-383]

Kajiwara et al., (2011), Experimental study on sorption and fractionation behaviors of rare metals (In, Ga) and toxic elements (As, Pb) in acidic river. [Shigenchishitsu 61 (3), (2011), 167-180] (in Japanese with English abstract)

Keywords: rare metal elements, rare earth elements, man-made ore deposit, acid hot spring

## Control factors for concentrations of elements dissolved in acid hot-spring waters

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Volcanic-magmatic-hydrothermal systems can cause effective heat and mass transports from deep to shallow environments, and provide us potential hot spring resources, mineral resources and geothermal energy resources. In order to enjoy such benefits from the systems, it is necessary to understand physico-chemical conditions of heat and mass transport processes in the systems. For this purpose, acid hot-spring waters were sampled and analyzed, and sources of each element dissolved in the waters and controlling factors of the concentrations were examined in this study.

Elements dissolved in the waters exhibit negative correlations of concentrations to pH. The elements were classified into four following groups. Group-I (S, Cl) derive from magmatic fluids. Group-II (B, F, As, Br, Cd, In, Sb, I, Tl, Pb) also derive mainly from magmatic fluids and partly from other sources (at least for B, As, I). Group-III (Li, Na, Mg, Al, Si, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, Ge, Rb, Sr, Y, Cs, Ba, REEs, Mo, W, U) derive from rocks through congruent dissolution. And Group-IV (P, Ti, Zr) were insoluble elements. Some elements (Be, Bi, Hf, Th, Cu, Se, Ag, Sn, Au) were not classified due to low concentrations below detection limits of analyses.

Factors controlling concentrations of elements recognized were followings: (a) dilution of magmatic fluids by meteoric water (deduced from hydrogen-oxygen isotope values of waters and negative correlations of concentrations versus pH), (b) potential transition of oxidation/reduction potentials of fluids (implied by concentrations close to sulfide solubilities for Cd, Zn, Pb and Tl), (c) addition of elements derived from precipitates in ancient hydrothermal activities (deduced from higher ratios of As/Cl, Br/Cl and I/Cl in fluids than high-temperature volcanic gases), (d) potential depositions of minerals (implied by supersaturation conditions of waters with respect to minerals for Si to quartz and Al to kaolinite and alunite, saturation index close to zero for Ba to barite, and apparent low concentrations for Group-III (P, Ti, Zr) and concentrations below detection limits for Be, Bi, Hf, Th, Cu, Se, Ag, Sn, Au). Based on these lines of evidence, a transport model for each element in volcanic-magmatic-hydrothermal system was tentatively constructed.

This study might be helpful for future planning of exploration target of metal resources and exploitation of geothermal energy resources toward the central parts of volcanic-magmatic-hydrothermal systems.

Keywords: acid hot springs, dissolved elements, concentrations, control factors