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論文内容要旨

Volcanic-magmatic-hydrothermal systems can cause effective heat and mass transports from deep to shallow environments, providing us potential geothermal energy resources and mineral 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. Acid hot-springs (pH<4) commonly occur in central parts of the systems, where discharges of magmatic fluids occur after water/rock interactions and mixing with meteoric water at varied degrees during ascend. As a result, four following types of acid hot-spring waters are produced: HCl-type (chloride-rich acid sulfate-chloride water), SO₄-type (sulfate-rich acid sulfate-chloride water), H₂S-type (steam-heated acid sulfate ground water), and NaCl-type (steam-heated acid sulfate ground water mixed with neutral pH chloride water). Geochemical investigations of these acid hot-spring waters are available for revealing physico-chemical conditions of interiors of volcanic-magmatic-hydrothermal systems. Thus, three following subjects to be elucidated were posed in this dissertation: (1) role of geological structures to genesis of acid hot-spring water types, (2) sources of each element dissolved in acid hot-spring waters and controlling factors of concentrations, and (3) chemical resources potentials of acid hot-spring waters.

In this study, acid hot-spring waters were sampled from fourteen following areas: HCl-types from Tamagawa(TM) and Kawarage(KR), SO₄-types from Kawayu(KW), Esan(ES), Sukayu(SK), Sukawa(SW), Zao(ZO), Kusatsu(KS) and Manza(MN), H₂S-types from Fukenoyu(FK), Goshogake(GS), Onikobe(ON) and Hakone(HK), and NaCl-type from Noboribetsu(NB). Temperature, pH, electric conductivity, oxidation/reduction potential of waters discharged were measured in site. Major to trace element compositions were analyzed using ion chromatography methods, inductively coupled plasma atomic emission spectrometer and inductively coupled

plasma mass spectrometer. Oxygen and hydrogen isotope ratios of waters were measured using mass spectrometers. Saturation degrees of waters to various minerals and speciation of elements in waters were calculated using geochemist's workbench numerical-simulation software.

Results of this study were summarized as follows with most focus on the HCl- and SO₄-type waters. HCl-type waters have high discharge temperatures (96-98°C) with low pH (1.3-1.6) in contrast to SO₄-type waters having low discharge temperatures (40-94°C) with high pH (1.1-3.2). The HCl-type waters exhibit heavy δD and $\delta^{18}O$ values, indicating mixing of magmatic fluids (contribution of about 20%) with meteoric water, while SO₄-type waters exhibit the values close to those of local meteoric water. Oxidation/reduction potentials of waters measured show a large variation, but some values (0.1-0.4V) implied controls by oxidized/reduced sulfur species rather than ferrous/ferric iron species, although no obvious difference was recognized between HCl- and SO₄-type waters. HCl-type waters contain a larger amount of anions than cations, while SO₄-type waters sometimes indicate amounts of anions close to cations, suggesting slight progress in neutralization through water/rock interaction in SO₄-type waters than HCl-type waters. Li/Cl-F/Cl ratios of waters also implied progress in neutralization of some SO₄-type waters rather than HCl-type waters. Most of minor to trace elements in waters exhibit negative correlations of concentrations to pH, implying dilution of waters as a common factor controlling concentrations and pH. Geochemical simulations suggested that HCl-type waters have undergone water/rock interactions at high temperatures (220-270°C) in contrast to SO₄-type waters at low temperatures (70-270°C).

(1) First subject is recognition of role of geological structures to genesis of acid hot-spring water types. TM and KR springs discharging HCl-type waters occur at a caldera rim and in subsided zone, respectively, where the vertical fractures are expected to develop. Similar geological structures were found in SK spring discharging SO₄-type water and ON spring discharging H₂S-type water (a caldera rim and horst zone, respectively). Such vertical fractures can work as conduits for either magmatic fluids to ascend (TM and KR springs) or meteoric water to descend (SK and ON springs). In former case, high-temperature magmatic fluids are likely to cause boiling from deep levels, while in latter case, magmatic fluids are restrained from boiling by mixing with deeply circulating low-temperature meteoric water. Sulfur species (SO₂, H₂S) are generally less soluble in waters than chloride (HCl). Then, fluids possibly decrease in S/Cl ratio through boiling, resulting in HCl-type waters, while SO₄-type waters seem to preserve S/Cl ratios of initial magmatic fluids. Geothermal reservoir has been already formed at deep levels beneath ON spring, and magmatic fluids ascended are trapped in the reservoir, resulting in

permission of H₂S-rich vapor without chloride to ascend to the surface. These lines of consideration suggested a change in role of geological structures during evolution of hydrothermal systems.

Magmatic fluids ascended to shallower levels have either opportunity to cause boiling or undergo mixing with meteoric water. SO₄-type waters in KS and ZO springs are formed at bottom levels of volcanos, which might be shallower than the above-mentioned vertical-fracture structures. Then, magmatic fluids ascended encounter a large amount of meteoric water because of highly permeable overlain volcanic rocks, and are restrained from boiling, resulting in SO₄-type waters in the springs. However, it is difficult to prevent fluids from boiling at a central part of fluid upflow zone in KS area. Thus, geological structures seem to influence on the depths and amounts of magmatic fluids mixed with meteoric waters, partly contributing to differentiation of acid hot-spring water types.

(2) Second subject is elucidation of sources of elements and controlling factors of their concentrations. Elements dissolved in acid hot-spring waters were classified into four following groups based on normalized values of their concentrations by chemical compositions of a standard andesite rock (JA1): Group-I with high normalized values (S, Cl). Group-II with slightly high values (B, F, As, Br, Cd, In, Sb, I, Tl, Pb), Group-III with values similar to each other (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), and Group-IV with low values (P, Ti, Zr). Some elements (Be, Bi, Hf, Th, Cu, Se, Ag, Sn, Au) were not classified due to small numbers of analyzed data or concentrations below detection limits of analysis. Referring chemical compositions of volcanic gases in previous publications, Group-I derive from magmatic fluids, Group-II also derive mainly from magmatic fluids and partly from other sources (at least for B, As, I), and Group-III derive from rocks through congruent dissolution. Factors controlling element concentrations recognized were followings: (a) dilution of magmatic fluids by meteoric water (deduced from δD - $\delta^{18}O$ 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 volcanic gases), (d) potential depositions of minerals (implied by supersaturation of waters with respect to minerals for Si to quartz and Al to kaolinite, saturation index close to zero for Ba to barite, and apparent low normalized values for P, Ti, Zr, and concentrations below detection limits of analysis for Be, Bi, Hf, Th, Cu, Se, Ag, Sn, Au).

(3) Third subject is evaluation of chemical resources potentials of acid hot-spring waters. In general, acid hot-spring water is characterized by their low pH, which indicates high ability for dissolving rocks. Annual amounts of elements discharged from acid hot-springs were calculated, and compared to market prices of mineral resources and domestic consumptions. Annual amounts are calculated to be about 10^5 - 10^7 (kg/year) for elements of less than 20th atomic numbers, 10^2 - 10^7 (kg/year) for elements of 20th to 40th atomic numbers, and below 10^2 for elements of more than 40th atomic numbers. The V, Sc, Ga and REEs exhibit high market prices and/or high supplement ratios to domestic consumptions. Thus, recovery of these elements should be considered in the next step, in which the coupling of recovery techniques with neutralization processes of acid hot-spring waters and binary geothermal power generation systems might be economically advantageous. Other elements dissolved in acid hot-spring waters appear to have no advantage as metal resources from short-term perspective, but they might have deposited at specific places downstream for a long time. It is necessary to investigate whether or not such specific deposition places are present in a future study.

These results of this dissertation might be helpful for understanding the heat and mass transport processes in volcanic-magmatic-hydrothermal system, future exploitation of geothermal energy resources toward volcanic to magmatic circumstances, and future planning of exploration target of metal resources related to acid hot-spring waters.

論文審査結果の要旨

火山国である本邦には多くの温泉が分布している。温泉は大局的には火山帯の中心部から周辺部にむかって、酸性泉、中性塩化物泉、炭酸水素塩泉と泉質の異なる温泉が累帯分布する。酸性泉は火山体の中心部に位置し、火山-マグマ-熱水系の時間的、空間的発達過程を考察するうえで重要な役割を果たしている。酸性泉に関する研究は古くから行われているが、酸性泉の分析、分類が主目的で、資源性に関する検討は遅れていた。本研究は、本邦に分布する 14 の代表的な酸性泉について現地調査を行い、酸性泉の溶存成分の地化学特性を解明し、併せて地質構造や発達過程の解析から、資源ポテンシャルに関する考察を加えたもので全編 5 章よりなる。

第 1 章は緒論であり、研究の背景と本研究の目的を述べている。

第 2 章は、調査をした 14 の酸性泉について、地質、火山、温泉の概要を示し、温泉水の主成分組成から、酸性泉を HCl 型、SO₄ 型、H₂S 型および NaCl 型の 4 つに分類し、それぞれの泉質の特徴について述べている。さらに酸素・水素安定同位体組成から、マグマ水の寄与、天水の混合、沸騰現象の有無等についての考察を進めている。また、地化学的数値解析手法を用いて、酸性泉の深部環境を推定し、各泉質と地質構造との関係を明らかにしている。その結果、HCl 型は、高温かつ低い pH であり、マグマ性流体の寄与が大きく、高角断裂系が発達する地域に分布し、この高角断裂系はマグマ性流体の上昇路として機能するとともに、高温の熱水が深所から浅所の広い深度範囲にわたって沸騰を生じる環境であったと推定された。これに対して、SO₄ 型は相対的に湧出温度が低く、また pH がやや高めであり、マグマ性流体の寄与が認められないことが多く、さらに天水との混合が進んで熱水の沸騰が抑制された環境下で形成されたと考えられた。H₂S 型および NaCl 型は相対的に高温で、高い pH であり、H₂S 型は深部に賦存する熱水から脱気した H₂S 成分が浅所で酸化されて形成され、NaCl 型はこのような H₂S 型の熱水が元の中性塩化物熱水と混合したものと解釈された。

酸性泉のうち、特に代表的な HCl 型と SO₄ 型の生成環境の差異を、はじめて系統的に明らかにしたもので、これは、本研究を代表する大きな成果である。

第 3 章は、溶存成分の地化学特性を明らかにしたもので、希土類元素を含む微量成分全般についての分析を行い、濃度範囲、岩石組成および火山ガス組成との比較から溶存成分の濃度の規制要因についての考察を進めている。その結果、溶存成分を、マグマ性流体に由来し、酸性泉の泉質型を特徴づける成分、マグマ性流体や火山ガスに由来する成分、岩石の溶解に由来する成分、他の起源に由来する成分に分類し、その成果をまとめて酸性泉の各成分の移行過程のモデルを提唱した。これは、酸性泉の資源性とその元素の成因を考察する上で有用な成果である。

第 4 章は、酸性泉の資源性を、湧出量、溶存成分の濃度、国内消費量および現在の価格などをもとに考察し、短期的実利資源と長期的戦略的資源の意義を明らかにしている。この成果は、温泉水として放出されている有用元素の資源性を評価した初めての試みであり、希少資源確保の戦略立案に有効な指針を与えている。

第 5 章は、結論である。

以上要するに、本論文は、酸性泉の地化学特性を解明して、溶存成分の特徴や酸性泉の生成環境と発達過程を解析し、酸性泉の溶存成分の資源性について新たな知見を得たもので、地球化学、資源開発工学ならびに環境科学の発展に資するところが少なくない。

よって、本論文は博士(学術)の学位論文として合格と認める。