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授与した学位	博　士
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学位授与の要件	自然科学研究科物質科学専攻 （学位規則第４条第１項該当）
学位論文の題目	Development of precise analytical techniques for major and trace element concentrations in rock samples and their applications to the Hishikari Gold Mine, southern Kyusyu, Japan （岩石を構成する主要及び微量元素の高精度定量分析法の開発と南九州・菱刈金鉱床への応用）
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学位論文内容の要旨

Precise analytical techniques for major and trace element concentrations in rock samples have been established, and applied to the Hishikari Gold Mine together with Sr, Nd, Pb and B isotope systematics, in order to deepen our understanding of hydrothermal processes involved in the formation of gold deposits in the crust.

A precise method for simultaneous quantitative analyses of ten major (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P) and two minor (Cr and Ni) elements in silicate rock samples has been developed by using X-ray fluorescence spectrometry (XRF) on fused glass beads. H_2O^+, H_2O^-, and Fe^{3+}/Fe^{2+} ratio were also determined by the improved gravimetric and titrimetric methods in this study, respectively. The major element analyses by XRF together with wet chemical determinations of H_2O^+, H_2O^-, and Fe^{3+}/Fe^{2+} consequently provided the total major compositions to be 100 ± 0.5 wt.% in most silicate rock chemistry ranging from ultramafic to rhyolitic compositions.

In the acid digestion of crustal rock samples, it was first found that an aluminum fluoride, AlF_3, forms. This makes fatal interference in the trace element and isotope analyses employing ICP-MS and ID-TIMS, because AlF_3 extensively incorporates trace elements, and can not be decomposed by conventional methods such as evaporation of F with $HClO_4$. To overcome these problems, I have developed a new method to suppress the AlF_3 formation by adding excess Mg to a sample prior to acid digestion using Teflon bomb. This new method entirely suppressed the formation of AlF_3 and thus successfully achieved to accurate quantitative analyses of the trace element compositions of high-Al rock samples such as rhyolite and granite.

These analytical techniques developed in this study were applied to the samples from Hishikari Gold Mine together with B, Sr, Nd and Pb isotope systematics in order to investigate the origin and evolution of ore-forming fluid associated with gold deposits. The B-Sr-Nd-Pb isotopic compositions of volcanic rocks are significantly uniform, but clearly different from those of Shimanto sedimentary rocks. The Sr and Pb isotopic compositions of vein samples vary within the range between those of the volcanic and sedimentary rocks. This suggests that the Sr and Pb compositions of vein samples represent a two-component mixing caused by the involvement of volcanic rock and Shimanto sedimentary rock components as end member. In contrast, Nd isotopic compositions of two vein samples are clearly distinctive, and similar to those of their host rocks, volcanics and Shimanto Supergroup sediments. Such diversity in the Nd isotopic composition indicates that the Nd isotopic compositions of veins are attributed to unconfined aquifers equivalent to ore-forming fluids, which have been developed in the sedimentary rock and volcanic rock, because Nd concentrations in the fluids must be extremely low compared to the host rocks and thus the Nd isotopic compositions in the ore-forming fluids susceptibly inherit the isotopic compositions of the host rocks. On the contrary, the B-Pb isotope systematics of vein samples suggest that the volcanic component in the ore-forming fluid was mostly derived from high-temperature magmatic fluid liberated from an intrusive magma beneath the Shimanto Supergroup, and circulated meteoric water through fluid-rock interaction with volcanic rocks was not essentials in the formation of ore-forming fluid. This is also supported by the mass balance of gold in the Hishikari area. Because as much as 250t Au in the deposit can not be collected from country rocks (~1ppb) by possible scale of the hydrothermal circulation. In the formation of the low-sulfidation type epithermal gold deposit, the intrusive magma is considered to have played an important role of not only a heat source of hydrothermal system but also the source of the gold.

論文審査結果の要旨

論文提出者は、菱刈金鉱床生成に関わった熱水及び金の起源を理解するために、岩石中の高精度主要・微量元素組成分析法を確立し、鉱床を構成する石英脈及び鉱床周辺の堆積岩と火山岩類に対して、これらの元素定量分析とともにストロンチウム(Sr)、ネオジム(Nd)、鉛(Pb)並びにホウ素(B)同位体分析を行い、浅熱水性金鉱床の成因を明らかにした。

XRFを用いた岩石試料の主要元素組成定量分析において、分析条件の最適化を詳細に行うとともに、吸着水・構造水及び$Fe3^+/Fe2^+$を湿式分析法で求めることによって、分析精度を湿式重量分析法に匹敵するレベルに向上させることができた。

岩石中の微量元素組成や同位体組成をICP-MSやTIMSを用いて分析する際、試料の分解はフッ化水素酸を用いて行われるが、強い耐酸性を示すジルコンを含む岩石試料の場合、200℃以上でテフロン密閉容器を用いて行われる。しかし、従来方ではAlF_3が酸分解過程で生成し、微量元素分析時の回収率を著しく低下させるだけでなく、同位体希釈法においても同位体平衡を妨げ測定値に大きな誤差を生じさせることを発見した。論文提出者は、岩石中の(Mg+Ca)/Al比が1以下の場合にAlF_3が生成されることを見出し、分解時にMgを添加すればAlF_3の生成が抑制され、微量元素を100％回収できる"Mg添加法"を開発した。このことによって、微量元素分析や年代測定における分析確度を飛躍的に向上させることができた。

論文提出者は、菱刈金鉱床を地殻における熱水流体による元素移動のモデル場ととらえ、上述の高精度分析法に基づいた主要・微量元素組成及びB-Sr-Nd-Pb multi-isotope systematicsを用いて解析を試みた。その結果、菱刈金鉱床の形成に関わった熱水流体（鉱液）にはマグマ起源の流体の影響が明瞭に示され、浅熱水性鉱床の形成において地下に貫入したマグマは、熱水系の熱源としてだけでなく、金のソースとしても重要であることが明らかになった。

これらの研究結果は、分析技術の革新はもとより、これまで不明な点が多かった金鉱床成因につき多くの知見をもたらすとともに、浅熱水性流体の成因一般についても理解を深めた点で価値の高いものであり、学位論文として十分に価値があると認めるものである。