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Dating of submarine hydrothermal deposits by ESR and U-series methods

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As interests in submarine massive sulfides as mineral resources increase, geochronological study of submarine ore deposits becomes more important. Formation of a large ore body requires long-time duration of hydrothermal activity. Moreover, a systematic geochronological study to reveal mineralization stages and sequences would provide an important key to explore submarine ore deposits. We focused on a chronological study of barite (BaSO₄) and developed an application of electron spin resonance (ESR) dating of barites. Barite is a sulfate mineral commonly occurred in submarine ore deposits, sometimes including substantial amount of radium that substitutes barium.

As a sample, we used a massive ore deposit collected from a submarine active hydrothermal field (in the southern Mariana backarc basin). This deposit grew rather horizontally to a few meters in length and about 15 cm in a diameter. A piece of slice with thicknees of about 5 cm was taken from the middle part of the deposit and cut into 13 pieces. Each piece was crushed and barite and spharelite were extracted by chemical and magnetic methods.

The ESR signal due to SO_3^- radical was observed in barite. The signal intensity increased with gamma ray dose. By extrapolating the dose response to the zero ordinate, the accumulated natural doses were obtained. The concentration of radium was obtained by the low background gamma ray spectroscopy using a gemanium semiconductor detector. The natural dose rates were calculated from the value. The ESR ages were obtained by dividing the accumulated natural doses by dose rates.

U-series ages were also obtained for these pieces using sulfide mineral mainly composed of sparelite and pyrite by mass spectroscopy. The ages were calculated from the disequiliburium between ²³⁴U and ²³⁰Th.

The ages obtained by these two methods were consistent within 30 %. The ages for these 13 pieces were grouped into two, one about 2500 years and the other about 1300 years.

The oxidation state of Hadean melts and implications for the composition of Earth's early atmosphere

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Zircon is an exceptionally durable mineral that retains primary chemistry for most elements from the time of igneous crystallization. Zircons are the only known terrestrial solids dating from the first 500 Ma of Earth history, and thus present a unique opportunity to constrain intensive petrological variables from Hadean (i.e. >3.85 Ga) melts that would otherwise be inaccessible. We report an experimental calibration that makes it possible to evaluate the oxygen fugacity of terrestrial melts prior to the Archean based on the incorporation of heterovalent Ce into zircon. Zircons were grown in a piston cylinder apparatus at 1 GPa and 900 to 1300°C from hydrous silicate melts (~72 wt% SiO₂) doped with La, Ce and Pr (±P). The melt Ce4+/Ce3+ ratio was controlled throughout the duration of the experiments by buffering the oxygen fugacity at values broadly covering the range observed in terrestrial and lunar magmas.

Application of this calibration to zircons from the Bishop Tuff magma chamber, mid-ocean ridge basalt residuals, and lunar grains yields average calculated oxygen fugacities broadly consistent with independent estimates. Furthermore, our results show that Hadean zircons crystallized in melts having average oxygen fugacities within error of the fayalite-magnetite-quartz buffer, including zircons with chemical characteristics consistent with an origin from a mantle-derived melt. The oxidation state of Hadean magmas may yield critical constraints on the speciation of volatile gases entering the atmosphere in the Hadean; results of our calibration are most consistent with H_2O , CO_2 , SO_2 , and N_2 gaseous species as early as 200 Ma after solar system formation.

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