

Silicon isotope zonings in synthesized silicon crystals

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Introduction

Isotopic composition of silicon materials has been rarely determined in spite of their wide use as semiconductor. Previously, it was reported that 0.2‰ depletion of $\delta^{30}\text{Si}$ was found near the end of a single FZ (floating zone) crystal of 268mm long by conventional isotope analysis [1]. Recent SIMS microanalysis further revealed 0.4‰ of silicon isotopic heterogeneity in the same crystal [2]. We have carried out experiments of crystal growth and evaporation from silicon melt, using an FZ instrument with in-situ observation system, to evaluate the partitioning across the crystal/melt and vapor/melt interfaces.

Experimental

Silicon crystals were synthesized with the FZ instrument. The growth conditions such as the growth and rotation rates were changed several times during the runs. Evaporation experiments were also conducted. Pressure in the FZ furnace tube was adjusted by a turbo-molecular pump and Ar gas injection. Silicon isotopic ratios of the run products were precisely determined using the ims-1270 SIMS with Faraday cup multi-collectors at the Geological Survey of Japan [2].

Results and discussion

Isotopic variations of more than 1‰ in $^{30}\text{Si}/^{28}\text{Si}$ ratios were observed in all the analyzed grown crystals. Although the $^{30}\text{Si}/^{28}\text{Si}$ zonings were complicated, the decreasing trend of the $^{30}\text{Si}/^{28}\text{Si}$ ratios was generally recognized over the grown crystals, especially in the quenching part. This strongly suggests that the fractionation factor between crystal and melt is larger than unity. We confirmed that the fractionation factor between vapor and melt was near unity under 10^5 Pa of Ar, which is identical condition to the crystal growth experiments. Therefore, the contribution of evaporation to the isotopic change in the grown crystal was not considerable. The SIMS microanalysis revealed isotopic zoning in the synthesized silicon crystals. It is inferred that the silicon isotopic ratios in the FZ silicon crystals always vary according to the growth conditions such as the growth and rotation rates, and the extent of supercooling of the melt as well as the equilibrium fractionation between the crystal and its melt.

References

- [1] Fujii K., Tanaka M., Nezu Y., Nakayama K., Fujimoto H., De Bièvre P. and Valkiers S., (1996), Abstr. 17th Japan Symposium Thermophysical Properties, 291-294. [2] Morishita Y., Kita N.T. and Togashi S., (2000), Secondary Ion Mass Spectrometry SIMS XII, Elsevier, 1003-1006.

High Precision ^{234}U - ^{230}Th Dating Using MC-ICPMS

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U-series dating using mass spectrometric techniques is now being widely applied in the Earth Sciences to problems ranging from climate change to hominoid evolution. Whilst TIMS methods have set the standard (e.g. Edwards et al., 1987), recent developments in MC-ICPMS (e.g. Luo et al., 1997) have shown that this is a viable alternative method, with the potential for more rapid as well as precise and accurate analyses.

For $^{234}\text{U}/^{235}\text{U}$ measurements, the main issues are abundance sensitivity and SEM/Faraday calibrations. Use of SEM/Faraday is the preferred method as it offers the greatest dynamic range. The SEM/Faraday yield is determined either within the sample from $^{235}\text{U}_{\text{sem}}/^{235}\text{U}_{\text{far}}$ or by using a reference standard. Using the new NEPTUNE MC-ICPMS the within run precision for $^{235}\text{U}_{\text{sem}}/^{235}\text{U}_{\text{far}}$ is $\sim 0.05\%$ and the longer-term daily drift is ~ 0.1 to 0.2% , which is also dependent on ion beam focussing. Thus rapid (~ 15 minute) static analyses of $^{234}\text{U}_{\text{sem}}/^{235}\text{U}_{\text{far}}/^{238}\text{U}_{\text{far}}/^{233}\text{U}_{\text{far}}$ can be undertaken with an internal (2 sigma) precision of $<0.1\%$ but with an external precision $\times 2$ greater. Higher external precision ($<0.1\%$) requires internal yield calibrations as well as attention to dead-time corrections. At normal resolution, the abundance sensitivity of the NEPTUNE is ~ 20 ppm (at ^{237}U) with a contribution to ^{234}U of $\sim 0.2\%$. Thus the high abundance filter (RPQ) is utilised with order of magnitude (2 ppm) improvement and tailing to ^{234}U and ^{235}U being undetectable.

For Th, both ^{229}Th and ^{230}Th are measured in separate jumps on the ion counter, with mass fractionation corrections being undertaken with $^{235}\text{U}/^{238}\text{U}$. Discrimination between U and Th can however readily occur in the ICP plasma, which places some limitations on the use of $^{235}\text{U}/^{238}\text{U}$ to correct for Th mass fractionation. Precision for ^{230}Th measurements is generally better than 0.1% . In this study a standard GE nebuliser was used with an uptake of 50 ul/min. Without the aid of a desolvator, a 30 ppb solution gives ~ 2 volts of ^{238}U . Thus ~ 10 - 20 mg of coral, corresponding to ~ 30 - 60 ng of U, gives reproducible ages of better than ± 1000 years for last interglacial samples.

References

- Edwards R.L. Chen J.H. and Wasserburg G.J. (1987) Precise timing of the last interglacial period from mass spectrometric analysis of ^{230}Th in corals. *Science* **236**, 175-192.
Luo X., Rehkamber M., Lee D.-C. and Halliday A.N. (1979) High precision $^{230}\text{Th}/^{232}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$ measurements using energy-filtered ICP magnetic sector multiple collector mass spectrometry. *Int. J. MassSpectrom. Ion Process* **171**, 105-117.