行政院國家科學委員會專題研究計畫　成果報告

高精度珊瑚鈾釷定年技術及其古氣候重建之應用

計畫類別：個別型計畫
計畫編號：NSC92-2116-M-002-013-
執行期間：92 年 08 月 01 日至 93 年 09 月 30 日
執行單位：國立臺灣大學地質科學系暨研究所

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報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫可公開查詢

中　華　民　國 93 年 12 月 30 日

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NSC Project Reports

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中文摘要

92 年 8 月至 93 年 9 月期間，我們執行了一個個別型研究計畫"高精度珊瑚鈾釷定年技術及其古氣候重建之應用"，主要目的是將已成熟之高精度鈾釷分析技術，開發珊瑚標本的定年方法。為建立本技術，首先我們克服三項基本問題。第一，示蹤劑中的鈾釷同位素組成，特別是釷-230，已精確量測。第二，化學空白值已有效降低至只有 20 (±20) x 10^{-18} 克，僅相當於 1-2 個月的定年誤差。第三，珊瑚霰石骨骼成長過程中所沈積的初始釷-230 含量可利用等時線(isochron)技術推估。本研究初步成果顯示，我們的技術可提供比一年更好的定年精確及精準度。

釷-230 定年技術將繼續應用在南灣、蘇門達臘群島和萬那杜珊瑚標本及其它碳酸鹽標本上，並進一步應用在古氣候重建，海洋循環等領域。在計畫執行期間，我們總共發表十篇會議論文及三篇送審論文。

關鍵詞：釷-230、珊瑚、電漿質譜儀

Abstract

We executed a new project "High precision coral uranium-thorium dating technique and its application to paleoclimatic reconstruction" to apply our newly-developed high precision U-Th analytical techniques to date corals. We have solved three fundamental problems. First, the isotopic composition in spike solution has been quantified precisely. Second, procedural blanks have be reduced and characterized at these low levels. ^{230}Th procedural blank was only 20 (± 20) x 10^{-18} g, corresponding to an age uncertainty of 1-2-moths for coral ^{230}Th dating. Third, the initial ^{230}Th incorporated into growing aragonitic skeleton could be well evaluated using isochron techniques. The preliminary results demonstrate that the age precision offered by our techniques can be better than 1 year.

The developed ^{230}Th dating techniques will be continuously applied to corals collected from Nanwan, Sumatra Islands, and Vanuatu, and other carbonates. We had three refereed articles and ten conference papers published during the period of August 2003 – September 2004.

Keywords: ^{230}Th dating, coral, ICPMS

1. Rationale and propose

The combination of abundant geochemical tracers, weekly-to-monthly resolution, and applicability to both near-term and Pleistocene climatic changes provides coral as one of the richest of natural archives. Coral reefs are an important bridge between terrestrial and marine realms and can provide information in the coastal zone reflecting either land or ocean-based changes, or a combination of the two.

Since 1993, long-term and high resolution coral-inferred climate records have been published every year. However, faithful interpretation of environmental and paleoclimatic records relies on trustable and accuracy age control. Unfortunately, among the above applications, researchers encountered the same inevitable problem of chronological uncertainty. The age uncertainty is mostly attributable to the level of non-radiogenic ^{230}Th incorporated into growing skeleton (Cobb et al., 2003). This problem can be well constrained by building ^{230}Th/^{232}Th vs. ^{234}U/^{232}Th isochrons to estimate the initial content of non-radiogenic ^{230}Th.

2. Coral ^{230}Th dating techniques

The U-Th dating technique provides absolute chronological control for long-term tracer records in a single coral head or between corals from different locations. The best coral U-Th dating techniques could only provide a precision of 3 years for corals younger than 100 years (Edwards et al., 2003). To approach the establishment of high precision ^{230}Th dating techniques, we have solved two fundamental problems. First, the isotopic composition and ^{230}Th level in spike solution have been well quantified. Second, procedural blanks has been reduced and characterized at these low levels. ^{230}Th procedural blank has been effectively diminished to only 20 (± 20) x 10^{-18} g, corresponding to an age uncertainty of 1-2-moths. After overcoming the chemistry, the age uncertainty is mostly attributable to the level of non-radiogenic ^{230}Th incorporated into growing skeleton (Cobb et al., 2003). This issue can be well constrained by building ^{230}Th/^{232}Th vs. ^{234}U/^{232}Th isochrons to estimate the initial content of non-radiogenic ^{230}Th. Our preliminary results with Sumatran and Nanwan corals show that a precision better than one year can be achievable on ICPMS (Shen et al., 2002).

3. ^{230}Th dating on a Holocene speleothem

For most of speleothems, the initial Th associated with detrital materials into growing matrix can bias true ages, which play a pivotal role in paleo-sciences. Isochron diagram technique (Dorale et al., 2004) and development diagram (Cheng et al., 2000) were used on a stalagmite with high Th contamination collected from Ninh Binh, Vietnam, to evaluate the initial ^{230}Th values, ^{230}Th/^{232}Th ratios and ages.

With carbonate-detritus component analysis, a phenomenon of that the ^{230}Th migrates between calcitic and detrital phases is observed. The occurrence of ^{230}Th migration would be in (1) original rock or/and (2) chemical process. The results support the previous suggestion that the whole rock dissolution method is the best strategy for speleothem U-Th dating. When employing isochron diagram, two outcomes are shown: (1) on the same horizon discordant ages were obtained among sub-samples with an identical ^{230}Th/^{232}Th ratio; (2) among horizons different initial values of ^{230}Th/^{232}Th ratios and reverse ages were found. These observations support that there are many sources with different Th concentrations and ^{230}Th/^{232}Th ratios were introduced into a growing layer during crystallization. Kaolinite and illite would be like the principal Th carriers. Accordingly, the initial values of ^{230}Th/^{232}Th ratios were not identical not only between horizons, but also different loci on a single layer. Such heterogeneous co-precipitation of detrital materials forces that the simple two-dimensional isochron technique cannot be applied to these speleothems with significant and complicated Th contamination, which enhances the uncertainty of estimated ages. If development

diagram technique is also employed, the initial values of $^{230}Th/^{232}Th$ ratios are more constrained, varying from 17 to 26 ppm. The age of this stalagmite should be younger than 4300 years old.

4. Publications

Ten conference papers related to the developed high precision U-Th ICP-MS techniques have been presented in domestic and international conferences:

(1) Chiang, H.-W., **Shen C.-C.**, Chen Y.-G., and Chiu H.-I.. (2004) A preliminary study of seasonal variation during past twenty years by geochemical records in coral skeletons, Nanwan. *Annual Meeting, Chinese Geol. Soc.*, Abstract Volume, 63.

(2) Shen, C.-C., Chu M.-F., Lin H.-T., and Yu E.-F. (2004) Uranium isotopic and concentration measurements by quadrupole inductively coupled plasma mass spectrometry. *Xth Symposium on Quaternary of Taiwan and Environmental Changes of Taipei Basin*, Taipei, Taiwan, 5-6 December 2004., Abstract Volume, 106.

(3) Steinke, S., Chiu H.-I., Yu P.-S., **Shen C.-C**., Erlenkeuser H., and Chen M.-T. (2004) On the influence of sea-level and monsoon climate on the southern South China Sea freshwater budget during the last 18 kyrs. to be presented in the *8th International Conference on Paleoceanography*, Biarritz, France, 5-10 Sept 2004.

(4) Lee, H.-J., Liu K.-K., **Shen C.-C.** (2004) Effects of reduced Yangtze River discharge on the circulation of surrounding seas. *Workshop for 2004 Oceanographic Research Programs*, Abstract Volume, 14.

(5) Chiang, H.-W., **Shen C.-C.**, Chen Y.-G., and Fan T.-Y. (2004) A preliminary study of seasonal variation during past twenty years by geochemical records in coral skeletons, Nanwan. *Annual Meeting, Chinese Geol. Soc.*, Abstract Volume, 63.

(6) Chiu, H.-I, **Shen C.-C**., Chu M.-F., Chen M.-T., Wei K.-Y., and Steinke S. (2004) High-precision determination of Mg/Ca and Sr/Ca ratios in marine carbonates by cool plasma quadrupole ICPM. *Annual Meeting, Chinese Geol. Soc.*, Abstract Volume, 68.

(7) Li, K.-S., **Shen C.-C**., Sieh K., Wang X., Natawidjaja D., and Edwards R. L. (2004) Contemporary technique of young coral ^{230}Th dating and its limitation. *Annual Meeting, Chinese Geol. Soc.*, Abstract Volume, 41.

(8) Shen, C.-C., Lee T., Liu K.-K., Hsu H.-H., Wang C.-H., Lee M.-Y., Chen Y.-G., Lee H.-J. and Sun H.-T. (2004) Holocene precipitation in the southern Taiwan inferred from coral geochemical records. *Joint Geosciences Assembly* (*JGA*), 01-OB-009.

(9) Wang, X., Auler A. S., Edwards R. L., Cheng H., **Shen C.-C.**, Smart P. L., and Richards D. A. (2003) Millennial-scale ITCZ variability in the tropical Atlantic and dynamics of Amazonian Rain Forest. AGU Fall Meeting, San Francisco, USA, 08-12 December 2003.

(10) Shen, C.-C., Sung Y.-H., Chen Y.-G., Ho W.-K., Wang X., Galang C., Cheng H., Edwards R. L., Burr G. S., and Lam D. D. (2003) Initial ^{230}Th and isotopic compositions of U and Th in a Holocene stalagmite from Ninh Binh, Vietnam. AGU Fall Meeting, San Francisco, USA, 08-12 December 2003.

Three articles were published during this project period:

(1) Shen, C.-C., Cheng H., Edwards R. L., Moran S. B., Edmonds H. N., Hoff J. A., and Thomas R. B. (2003) Measurement of attogram quantities of ^{231}Pa in dissolved and particulate fractions of seawater by isotope dilution thermal ionization mass spectroscopy. *Analytical Chem.*, **75**, 1075-1079. (SCI)

(2) Dorale, J. A., Edwards R. L., Alexander E. C. Jr., **Shen C.-C.**, Richards D. A., and Cheng H. (2004) Uranium-series disequilibrium dating of speleothems: Current techniques, limits, and applications. *In*: Mylroie, J. and Sasowsky, I. D. (eds.), *Studies of Cave Sediments: Physical and Chemical Records of Paleoclimate, 177-197*, *Geol. Soc.*

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