

Compound-specific radiocarbon ages of biomarkers in the western North Pacific marginal sea sediments

M. UCHIDA¹, Y. SHIBATA², N. HARADA¹, N. AHAGON¹,
AND M. YONEDA²

¹Mutsu Institute for Oceanography (MIO), Japan Marine Science and Technology Center, Japan (uchidama@jamstec.go.jp)

²National Institute for Environmental Studies (NIES), Japan

Compound-specific radiocarbon analysis (CSRA) of organic compounds, as well as compound - specific isotope analysis, provide valuable information on the origin and carbon cycling in the biogeosphere. Age of the bulk organic matter in the marine sediments is difficult to be perfectly accepted as realistic age of sediment due to the reworking "relict" problem of organic material such as humic detritus and age uncertainty of organic components from marine and terrestrial sources.

We present results of the CSRA of individual compounds (biomarkers) isolated from surface sediments in the southern Okhotsk Sea and the western North Pacific. The radiocarbon ages of biomarkers such as fatty acids, hydrocarbon, sterols and long-chain ketones (alkenones) have been analysed in order to obtain information of not only the dates but also origin and carbon cycles of organic compounds in marine systems. In the western North Pacific marginal sea, the radiocarbon diversity of individual compounds from the sediment have been first investigated to explore the compound-specific radiocarbon chronology as the alternative dating proxy to foraminifera-based chronology. The three multiple core samples were recovered from southern and northern flanks across the Kurile islands between southern Okhotsk Sea and western North Pacific. (MC-02: 46°18'N, 152.32.E, water depth: 2796m, MC-03: 48°14'N, 151°59'E, 3245m, MC-04: 49°22'N, 153°00'E, 1822m) during the MR00-K01 and MR00-K03 cruises of JAMSTEC R/V Mirai. We have found large age variability among individual compounds of assuredly different origins from both autochthonous (marine) and allochthonous (terrestrial) products in the same horizon of sediment core. The dating approach of CSRA had several problems in relation to difficulties of recovering target compounds with higher purities and realistic amount from sediment samples, and extremely small amount AMS ¹⁴C analysis. However, to date we have achieved successfully these problems as the result of technical modifications of the PCGC system and graphitization of compounds for a microscale AMS analysis. Our results of CSRA using the bathyal sediments would provide the possibility as an chronology tool for estimating the age of sediment using organic matter for paleoceanographic study.

Age spectra of biotite as indicator of deformation rate: evidence from microchemical, structural, step-heating and laser ⁴⁰Ar/³⁹Ar analyses

UDIN D.¹, TRAVIN A.V.¹, VLADIMIROV V.G.²,
PROSTYAKOV K.¹, BARABASH N.V.²

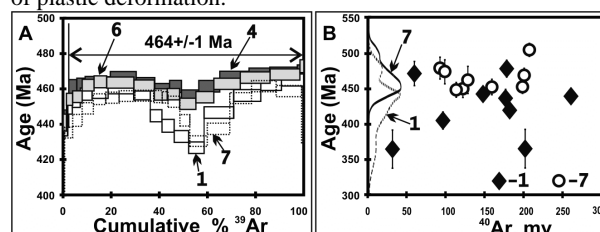
¹United Institute of Geology, Geophysics and Mineralogy, SB RAS, Novosibirsk, Russia, travin@uiggm.nsc.ru

²Institute of Geology SB RAS, Novosibirsk, Russia

Introduction and geological background

Micas are most often used for ⁴⁰Ar/³⁹Ar dating of deformation events yet dependence of age spectra shape from rate of deformation is not clear totally. This study examines relation between rate of deformation and ⁴⁰Ar/³⁹Ar isotope record in biotite. Samples were selected from metapelitic layer of uniform composition passing through rigid lithon (0.5 km in size) inside Ak-Dagskaya shear zone of Sangilen massif (South-East Tuva, Russia). Ductile deformations are collected on borders of such lithons composed from metapelitic rocks. Microstructures are expressed by S/C fabrics, shear bands indicating sinistral sense of shear. Metamorphic conditions calculated using Bt-Grn geothermometers correspond to the late HTLP (M2) event dated to be of 468±6 Ma (Petrova, Kostitsyn, 1997) with higher temperature on the lithon borders relatively to internal parts.

Figure 1. ⁴⁰Ar/³⁹Ar stepwise heating (A) and laser (B) data on biotite. Numbers 1 and 7 correspond to samples from opposite borders of lithon and are characterized by high deformation rate. Numbers 4 and 6 correspond to samples from internal part of the lithon and have not visible indications of plastic deformation.



Results and discussion

Step-heating of the bulk biotite separates (Fig. 1 A) yields spectra with staircase at low and depression at intermediate temperatures. The deformed samples (1, 7) yield much more expressed depression and noticeably younger ages all over the spectra. Dating on biotite grains of different size using pulsed ruby laser (size of the probe area – 50 micron) yield one mode age distribution for sample-7 (Fig. 1 A) with maximum at 455 Ma. At the same time sample-1 yields 3 mode age distribution with maximums at 475 Ma, 439 Ma and 366 Ma.

Digital modeling revealed that age spectra of all samples can be described well using model of superposition of at least two components of different age and grain size with lower age value corresponding to smaller grain size. The model is based on assumption that every component display plateau age spectra. Depression at intermediate temperatures is formed due to the fact that maximum of degassing of smaller grain size component is shifted towards lower temperatures.

New techniques for separation and analysis of Lu-Hf, Sm-Nd and the REE by MC-ICP-MS

DAVID ULFBECK¹, JOEL BAKER¹, MARTIN BIZZARRO²

¹Danish Lithosphere Centre, Øster Voldgade 10 L, 1350 Copenhagen K., Denmark

²Geological Museum, Øster Voldgade 5-7, 1350 Copenhagen K., Denmark

We have developed new techniques for rapid and reproducible analysis of the Lu-Hf and Sm-Nd isotopic systems, as well as ID analysis of the REE by MC-ICPMS. Samples for Lu-Hf and Sm-Nd isotopic analysis are fused with LiBO₄ and the melt is dissolved in weak HNO₃, spiked with ¹⁷⁶Lu-¹⁸⁰Hf and/or ¹⁴⁹Sm-¹⁵⁰Nd tracers. After a pre-concentration step for HFSE and REE by Fe-hydroxide coprecipitation, Lu and HFSE+REE cuts are recovered from a cation exchange column with 4 and 6 M HCl. Hf is separated from the HFSE+REE cut using TEVA-SPEC resin in high molarity HCL; the LREE may be saved from this step enabling Sm-Nd isotopic determinations on the same sample digestion. Hf yields are > 90% while total procedural blanks are < 100 pg (Hf) and < 10 pg (Lu), even for large (0.3 g) low-Hf samples with variable matrix compositions like meteorites, apatites and garnets. Multiple analyses of a range of Standard Reference Materials yields a reproducibility of < 0.2% on Lu/Hf ratios. Even difficult to digest samples only take two days to digest and separate Lu-Hf and Sm-Nd for analysis.

Samples for REE ID analysis are digested by standard acid digestion techniques. M-HREE and LREE are collected from a cation exchange column, which provides a M-HREE cut with sufficient separation from the LREE to render oxide interferences trivial, and a Ba-free LREE cut. Heavy, middle and light REE concentrations are determined by three 1-2 min analyses. Replicate digestions of international standards demonstrates that concentrations reproduce to < 1%, and inter-REE ratios reproduce to ≤ 0.2% (2 sd). Eu and Ce anomalies reproduce to < 0.15%. Mono-isotopic Pr can also be measured during the LREE isotope dilution run, by reference to Pr/Ce and Pr/Nd ratios measured in a REE standard solution. Pr concentrations determined in this way reproduce to < 1%, and Ce anomalies calculated using La and Pr also reproduce to < 0.15% (2 sd). The precise Ce (and Eu) anomaly measurements should allow greater use of these features in studying crust-mantle recycling, or redox-induced affects on the REE during recycling and dehydration of oceanic lithosphere, partial melting, metamorphism, alteration and/or sedimentation processes. This technique for measurement of the REE is superior in terms of the analytical reproducibility or rapidity of analysis compared with quadrupole ICP-MS or TIMS ID techniques and consumes sub-ng amounts of the REE. We will report on a high precision REE study of oceanic basalts and chondrites, particularly with respect to evaluating Ce anomaly variations in these materials.

Mg isotopic compositions of W-L and accretionary rims of CAIs

T. USHIKUBO, K. HIRAI AND H. HIYAGON

Department of Earth and Planetary Science, Graduateschool of Science, University of Tokyo, Tokyo, Japan
(ushi@space.eps.s.u-tokyo.ac.jp, khirai@space.eps.s.u-tokyo.ac.jp, hiyagon@eps.s.u-tokyo.ac.jp)

Introduction

It is known that common type CAIs such as Types A, B and C, which are frequently found in CV chondrites, have layered rim structures which are called as Wark-Lovering rims (W-L rims). W-L rims consist of three layers: spinel (and minor perovskite) layer, melilite (or its alteration products, e.g. anorthite, nepheline) layer and diopsidic pyroxene layer, from interior to exterior. It is also known that CAIs are sometimes surrounded by fine-grained mineral layers which are called as accretionary rims. Although ¹⁶O-rich signatures observed in W-L rims and accretionary rims suggest that the origin of these layers relates to the CAI formation event, it is not known how these rim structure formed. Here we present preliminary results of Mg isotopic measurements of interior, W-L rims and olivine in accretionary rims of CAIs.

Results and Discussions

Mg isotopic measurements were performed for two type A CAIs and two type B1 CAIs with an ion microprobe. Matrix effects were determined and corrected using terrestrial minerals. All CAIs have positively fractionated Mg isotopes in their interior with a fractionation factor, F_{Mg} , of +2 to +10‰/amu relative to PO chondrules (assuming $F_{Mg} \sim 0‰/amu$). F_{Mg} of spinel in the W-L rims is similar to that of spinel in the interior of CAIs. F_{Mg} of diopsidic pyroxene in the W-L rims and that of olivine in the accretionary rims, in contrast, are smaller than that in the interior of CAIs (-3 to +2‰/amu).

It is suggested that spinel in the W-L rims is closely related to (spinel in) the interior of CAIs. It is also suggested that diopsidic pyroxene in the W-L rims and olivine in the accretionary rims are different from the interior and spinel in the W-L rims of CAIs in view of Mg isotopes.

Recently, a flush heating process was proposed for the formation of W-L rims. It seems, however, difficult to explain the present results. We consider that spinel layer and pyroxene layer of W-L rims formed by separate processes and that the latter possibly formed by a condensation process.

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