
**Reconstruction of changes in the Southern Ocean Overturning
Circulation using radiogenic Pb and Nd isotopes in marine sediments
and a Fe-Mn crust for the past 19 Ma**

Dissertation
zur Erlangung des Doktorgrades
Dr. rer. nat.

der Mathematisch-Naturwissenschaftlichen Fakultät der
Christian-Albrechts-Universität zu Kiel

vorgelegt von
Huang Huang
Kiel, 2019

Gutacher und Betreuer: Prof. Dr. Anton Eisenhauer

2. Gutachter: Prof. Dr. Samuel Jaccard (Univ. Bern. Switzerland)

Eingereicht am:

Datum der Disputation: 28.10.2019

Zum Druck genehmigt:

gez. (Titel, Vor- und Zuname), Dekan

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Kiel, 2019

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Abstract

Radiogenic lead (Pb) and neodymium (Nd) isotopes are sensitive paleoceanographic proxies for the reconstruction of ocean circulation changes in the past. The goal of this dissertation is to develop improved approaches to recover past seawater Pb and Nd isotope signals from marine sediments and ferromanganese (Fe-Mn) crust, and apply it for tracing water mass sourcing changes in the Southern Ocean at (sub-)millennial resolution.

Chemical reductive leaching of hydrogenetic Fe-Mn oxyhydroxides from bulk marine sediments offers an efficient and easily accessible way to recover past seawater Pb and Nd isotope signatures. However, the leached seawater derived Pb and Nd isotope signal could be compromised if substantial quantities of Pb and Nd were released from non-hydrogenetic sediment fractions during leaching. In Chapter 3, a fast and reliable vortexing leaching method is presented for extracting porewater Pb and Nd isotope signals from sediment samples in the Atlantic sector of the Southern Ocean. The effect of a previously introduced $MgCl_2$ prewash is investigated, as well as the role of chelate ligands and length of leaching time. In order to validate the vortexing leaching method, Pb and Nd isotope signatures were analysed in actual seawater and underlying porewater and sediment leachates from three stations in front of the Filchner-Rønne Ice Shelf, Antarctica. The well-matching results between water sample and leachates corroborate the robustness of this method. Moreover, using the newly developed vortexing leaching method, I generated authigenic Pb and Nd isotopic maps from 70 Southern Ocean coretop sediment samples to help select suitable sites for paleoceanographic and paleoclimatic reconstructions.

In Chapter 4, seawater-derived downcore sedimentary Nd and Pb isotope records are presented from three Southern Ocean sites inside and outside the Weddell Sea to resolve changes in Southern Ocean overturning circulation for the past two glacial terminations. The data provide strong evidence for the absence of Weddell Sea

AABW outside the Weddell Sea during the last and penultimate glacial maximum. The successive southward displacement of the SO overturning cell following glacial maxima is recorded by increasing contributions of Weddell Sea derived Pb admixtures to regions outside the Weddell Sea during both glacial terminations. The export of Weddell Sea AABW resumed late during glacial terminations, coinciding with the last major atmospheric CO₂ rise in the transition to the Holocene and the Eemian. While Holocene AABW formation and export out of the Weddell Sea took place without major perturbations, our new records lend strong support for a previously inferred overturning stagnation event during the peak Eemian interglacial.

In Chapter 5, an unprecedented continuous high-resolution Pb isotope record was recovered from a Fe-Mn crust grown on the Marie Byrd Seamont in the Pacific sector of the Southern Ocean using laser ablation coupled MC-ICPMS. The Pb isotope data document the ACC history for the past 19 million years and indicate that the final establishment of clockwise (eastward) circulating Antarctic Circumpolar Currents took place at 14 Ma. The Pb isotopic evolution also suggest five large-scale ocean circulation reorganization events which are likely related to changes in Antarctic Bottom Water formation and tectonic events in ocean gateway regions, i.e. Panama Seaway and Drake Passage.

Overall, the results presented in this dissertation show deep sea Pb and Nd isotope records are able to resolve the changes in the glacial/interglacial Southern Ocean overturning circulation front shifting and the Antarctic Bottom Water evolution. The Pb isotope system also shows great potential in tracking Antarctic ice dynamics and ocean circulation changes on Cenozoic timescales. Applying these approaches employed in this dissertation to different key locations and into different time period will help resolving more ocean circulation mysteries.

Kurzzusammenfassung

Radiogene Blei- (Pb) und Neodynamium- (Nd) Isotopenverhältnisse sind sensitive paläozeanographische Werkzeuge für die Rekonstruktion von Ozeanzirkulationsmustern der Vergangenheit. Das Ziel dieser Doktorarbeit ist, einen verbesserten methodischen Ansatz zu entwickeln, um vergangene Pb- und Nd-Isotopensignale aus marinen Sedimenten und aus Eisenmangankrusten (Fe-Mn-Krusten) zu gewinnen und diese für die Rekonstruktion der Änderungen der Südozeans-Zirkulation mit einer zeitlichen Auflösung von bis zu unter tausend Jahren anzuwenden.

Das chemisch reduzierende Lösen von hydrogenetischen Fe-Mn Oxyhydroxiden aus marinen Sedimenten ist ein effizienter und einfacher Weg, um vergangene Pb- und Nd-Meerwasserisotopensignaturen zu gewinnen. Allerdings könnten die gelösten Pb- und Nd-Isotopensignale verfälscht werden, falls während des chemischen Lösungsvorgangs erhebliche Mengen an Pb und Nd aus nicht-hydrogenetischen Sedimentkomponenten gelöst werden. In Kapitel 3 wird eine schnelle und zuverlässige „Vortexing“-Lösungsmethode für die Extrahierung von Pb- und Nd-Isotopensignalen aus Sedimentproben des atlantischen Sektors des Südozeans präsentiert. Sowohl der Effekt einer vorherigen Vorreinigung mit $MgCl_2$ wird untersucht, als auch die Rolle von Chelatliganden und die Länge der Lösungsdauer. Um die „Vortexing“-Lösungsmethode zu validieren, wurden die Pb- und Nd-Isotopensignaturen in Meerwasserproben, sowie im sedimentären Porenwasser und in chemisch gelösten Fe-Mn Oxyhydroxiden an drei Stationen vor dem Filchner-Rønne-Eisschelf in der Antarktis analysiert und verglichen. Die gut zueinanderpassenden Ergebnisse zwischen Wasserproben und gelösten Fe-Mn Oxyhydroxiden belegen die Zuverlässigkeit dieser Methode. Zudem habe ich mithilfe der neu entwickelten „Vortexing“-Lösungsmethode authigene Pb- und Nd-Isotopenkarten mittels 70 Oberflächensedimentproben aus dem Südozean

generiert, die helfen sollen, geeignete Orte für paläozeanographische und paläoklimatische Rekonstruktionen auszuwählen.

In Kapitel 4 werden Meerwasser-Nd- und Pb-Isotopen datensätze aus Sedimentkernen präsentiert. Sie stammen von drei Südozeanlokalitäten innerhalb und außerhalb des Weddellmeeres und sollen Änderungen in der Südozean-Umwälzzirkulation der letzten zwei Deglaziationen aufzeigen. Die neuen Daten belegen die Abwesenheit von aus dem Weddellmeer stammenden Antarktischen Bodenwassers (AABW) im atlantischen Sektor des Südozeans während des letzten und vorletzten glazialen Maximums. Die schrittweise Verlagerung der Zirkulationszelle des Südozeans nach Süden im Anschluss an glaziale Maxima wird durch erhöhte Anteile von Pb-Beimischungen aus dem Weddellmeer in Regionen außerhalb des Weddellmeeres während beider Deglaziationen aufgezeichnet. Der Export von Weddellmeer-AABW setzte spät während der jeweiligen Deglaziationen wieder ein und ereignete sich zeitgleich mit dem letzten größeren Anstieg des atmosphärischen CO₂-Gehalts während des Überganges ins Holozän und in die Eem-Warmzeit. Während die Bildung und der Export Antarktischen Bodenwassers aus dem Weddellmeer während des Holozäns ohne größere Störungen erfolgte, bekräftigen die neuen Datensätze eine frühere Studie, laut derer sich eine Stagnation des AABW-Exports aus dem Weddellmeer während des Höhepunktes des Eem-Interglazials ereignete.

In Kapitel 5 wurde ein bisher einmaliger kontinuierlicher Pb-Isotopen datensatz in hoher zeitlicher Auflösung aus einer Fe-Mn-Kruste gewonnen, die von dem Marie Byrd Seamount im pazifischen Sektor des Südozeans stammt. Dieser Datensatz wurde mit Hilfe einer Laserablations-Methode, gekoppelt an ein Multikollektor-Massenspektrometer, gemessen. Die Pb-Isotopen daten dokumentieren die Entwicklung des Antarktischen Zirkumpolarstroms während der letzten 19 Millionen Jahre und belegen die Etablierung des im Uhrzeigersinn (ostwärts) fließenden Antarktischen Zirkumpolarstroms vor 14 Ma. Die Pb-Isotopenentwicklung deutet außerdem auf fünf umfassende regionale Zirkulationsänderungen im

pazifischen Sektion des Südozeans hin. Diese stehen wahrscheinlich mit der Entstehung des Rossmeer-Tiefenwassers und tektonischen Ereignissen in Ozean-Gateway-Regionen wie der Schließung des Panamaseewegs und der Öffnung der Drakepassage in Verbindung.

Insgesamt erlauben die in dieser Doktorarbeit präsentierten Ergebnisse Einblicke in die deglazialen Änderungen der Zirkulation des Südozeans mithilfe einer Kombination aus tiefmarinen Pb- und Nd-Isotopen datensätzen. Das Pb-Isotopensystem birgt zudem großes Potential, um die antarktische Eisdynamik sowie känozoische Ozeanzirkulationsänderungen nachzuverfolgen. Die Anwendung der in dieser Doktorarbeit verwendeten Ansätze auf verschiedene Schlüssellokationen und auf verschiedene Zeitspannen kann helfen, weitere Rätsel der Ozeanzirkulation zu lösen.

Acknowledgements

First and foremost I want to thank my advisor Marcus Gutjahr. He is a dedicated and modest scientist model which I wish oneday I can shape myself into. I appreciate all his contributions of time, ideas, and effort to make my Ph.D. experience productive and stimulating. His office door is constantly open and he is always very patient with my daily basic questions since the beginning of my Ph.D study. Whenever I have an abstract or manuscript asking him for comments or revisions, he can quickly and properly give me feedbacks. I really enjoyed sharing the carbin with Marcus during Polarstern cruise PS111 in 2018 and am grateful to his help when the sea sickness took me down.

I want to thank my advisor Anton Eisenhauer for welcoming me as a member of his group and providing funding to support my Ph.D. study. He secured the free research environment around me which plays an essential role in my scientific work in GROMAR. I also benefit from his scientific advice and his group has been a source of friendships as well as collaboration during my Ph.D. study.

I am especially grateful of the support from my co-advisor Gerhard Kuhn. He invited me twice for Polarstern cruises to the Weddell Sea where the scenery is phenomenal. I couldn't even image me to have this fantastic life experience before I came to Germany. He also kindly provided me important sediment samples which are the foundation of my Ph.D. work.

It's my honour to have Martin Frank as my co-advisor as well. He has been always very supportive, and especially in the last two years he offered me a lot help during paper revisions and Fe-Mn crust dating.

I would like to thank Sam Jaccard for giving me important comments and suggestions for my first manuscript. Also, it is a great pleasure to have you as my external examiner.

I would like to thank all the members in our research group. I need to firstly give many thanks to Tyler Goepfert for his outstanding technical assistance and also for being a wonderful neighbour of mine. I also benefited a lot from the discussion with Jan Fietzke when he was having a cigarette in the smoking hotspot. I really appreciate the lab support and the concentration measurements by Ana Kolevica. I enjoyed the time spent with Volker Liebetrau, Florian Böhm and Isabelle Taubner no matter for scientific topics or dinners in the restaurants in Kiel.

With great appreciation I shall acknowledge Ed Hathorne and Christian Schlosser for their help of seaFAST measurement, and Chris Siebert for giving me the lab introduction tours at my first arrival. I also want to thank Sevasti Modestou for kindly providing me the USGS NOD standard pellets for my laser ablation work, Mario Thöner for the microprobe measurement. and Lisa Bretschneider for helping me translate the abstract into German.

In the end, I am grateful to my parents and friends. They always gave me enough support, encouragement and motivation to accomplish my goals.