EOS
EOS, TRANSACTIONS, AMERICAN GEOPHYSICAL UNION

VOLUME 92 NUMBER 26
28 JUNE 2011
PAGES 217–224

Ocean Margins: The Missing Term in Oceanic Element Budgets?

PAGES 217–218

The amount of carbon dioxide (CO_2) in the atmosphere is a function of many interrelated processes in atmospheric, oceanic, hydrological, biological, and human realms. Constraining the contributions of these realms to global carbon budgets hinges on knowledge of the ocean's role in carbon cycling, which in turn depends on the ocean's chemical state and biological activity. Both are dependent on element and nutrient inputs from continental sources—the more elements that reach the ocean in a form readily consumable by life, the more productive micro-organisms that form the foundation of the ocean's food supply can be.

Thus, on a fundamental level it is important to know how and where continental inputs reach the ocean. Fluxes traditionally considered in seawater element budgets are dissolved river inputs, dissolution of atmospheric dust, hydrothermal inputs, diffusive fluxes from deep-sea sediments, and submarine groundwater discharge. Interestingly, though most of the marine element budgets include a provision for small contributions from dust dissolution [*Jickells et al.*, 2005], the dissolution of solids deposited along the ocean margins is usually ignored. Yet recent studies show that sediments on continental slopes and shelves contribute significantly to the dissolved elements found in seawater. Tracing and understanding these contributions will help scientists to get a better picture of ocean circulation, biological productivity, and carbon cycling.

Evidence for Ocean Margins as a Source of Dissolved Elements

The world's deltas and estuaries act like fluidized bed reactors that are reworked for days to years, allowing sustained interaction with seawater and the potential for dissolution and precipitation of transported particulates. The annual global river discharge of suspended particulates likely exceeds 19×10^{15} grams per year [*Peucker-Ehrenbrink*, 2009], about 50 times the global dust input to the ocean (0.45×10^{15} grams per year [*Jickells et al.*, 2005]). This estimate of suspended particulate matter transported by rivers to the ocean most likely represents the lower limit, as it probably underestimates contributions from small rivers as well as coastal and glacial erosion.

Nonetheless, the fact that calculations of ocean element budgets typically factor in small contributions from dust implies that release to seawater of even a small fraction of the material deposited along the ocean margins could also significantly affect biogeochemical cycles. Also, the rate of bedrock erosion along the continent-ocean interface is likely an important factor controlling sediment sources at ocean margins [*Peucker-Ehrenbrink et al.*, 2010]. Constraining the importance of this source of continent-derived elements to seawater could therefore considerably modify scientific understanding of the modern ocean and its response to global changes in the past and future, because such submarine weathering might act on long timescales.

But how is the importance of this sediment release evaluated? Several recent publications have tackled this question. For example, the oceanic distribution of neodymium (Nd) isotopes and concentrations suggests that about 1–3% of the continental sediments deposited annually along ocean margins release elements to seawater through dissolution processes [*Arsouze et al.*, 2009; *Lacan and Jeandel*, 2005]. This result is consistent with observations made in estuarine sediments, suggesting that continental shelves and slopes are good settings through which

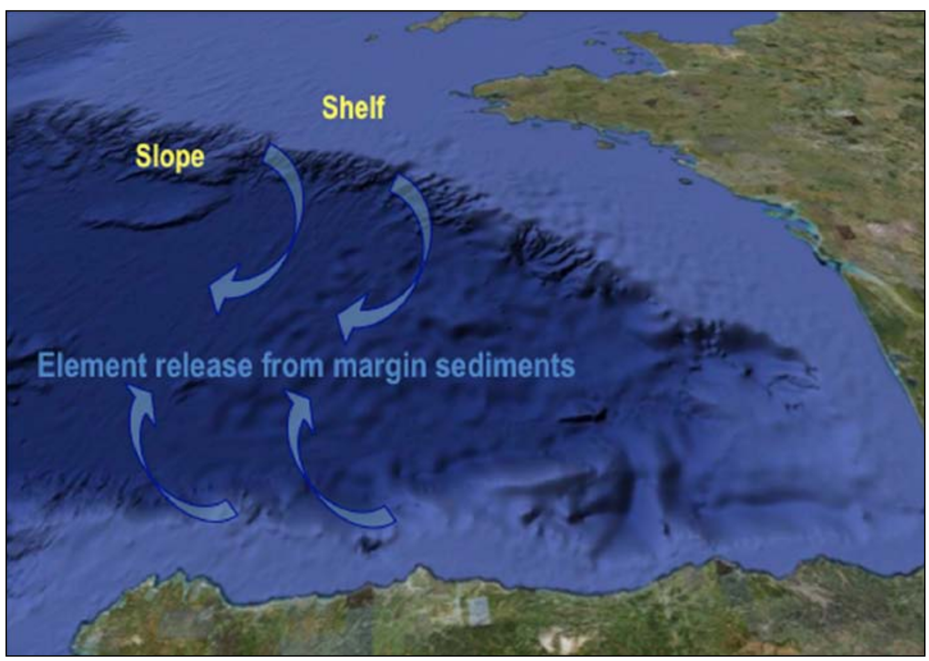

Fig. 1. Isotopes of neodymium, silicon, iron, and radium, as well as dissolved concentrations of rare earth elements, iron, or barium, reveal that release from sediment deposited on oceanic margins can be a significant source for dissolved elements in seawater; processes yielding this release need to be understood (e.g., submarine storms generating particle clouds called nepheloids could enhance release). The Bay of Biscaye is shown here as an illustration, but these processes are suspected to occur widely. This potentially important source has to be taken into account in oceanic budgets and climate models. Google Earth™ imagery ©Google™ Inc. Used with permission.

By C. Jeandel, B. Peucker-Ehrenbrink, M. T. Jones, C. R. Pearce, E. H. Oelkers, Y. Godderis, F. Lacan, O. Aumont, and T. Arsouze

sediments and/or suspended sediments dissolve, supplying rare earth elements (REE), such as Nd, to the ocean [*Sholkovitz and Szymczak*, 2000]. Results from batch experiments with seawater conducted on riverine, estuarine, and shelf sediments confirm significant REE exchange [*Jeandel et al.*, 2011]. Additionally, studies of dissolved versus suspended calcium (Ca) transport in rivers suggest that fluxes from ocean margins and from rivers are comparable in magnitude, affecting the carbon cycle through formation of marine Ca carbonate [*Berner and Berner*, 1996; *Gislason et al.*, 2008]. Similarly, results of batch experiments mixing basaltic particles and seawater indicate that significant amounts of silicon (Si) and strontium (Sr) could be released from continental particles within months [*Oelkers et al.*, 2011], thereby likely providing as yet unrecognized fluxes of continental Si and Sr input to seawater.

Several modeling studies suggest that sedimentary sources and mineral dust contribute equally to seawater concentrations of dissolved iron (Fe), another important marine micronutrient [*Moore and Braucher*, 2008; *Tagliabue et al.*, 2010]. However, studies of benthic fluxes suggest that the input of dissolved Fe from continental shelf sediments is 2–10 times higher than that from mineral dust [*Elrod et al.*, 2004; *Thullner et al.*, 2010; *Jickells et al.*, 2005]. Fe fluxes may be even greater under oxygen-depleted conditions that enhance Fe solubility, such as along Oregon's continental shelves [*Severmann et al.*, 2010]. Nd, Si, and Fe isotopes measured close to a coast (or a margin) clearly indicate that the source of dissolved elements is lithogenic [*Lacan and Jeandel*, 2005; *Fripiat et al.*, 2011; *Radic et al.*, 2011].

Together, these studies provide compelling evidence for important contributions of sediment release along ocean margins to the geochemical and isotopic budgets of various elements in the oceans and pose the question of how this process affects those elements involved in carbon cycling and, hence, climate. Assuming, as deduced from Nd budget considerations, that this process affects congruently 1–3% of the sediment deposited on the margins and considering a large range of lithological composition of margin sediments, margins are estimated to supply 0.7–5.4 teramoles per year of Si to the ocean, which is 12–96% of that supplied by rivers. The same calculation shows that 0.06–0.8 teramoles per year of Ca and 0.07–0.8 teramoles per year of magnesium (Mg) are supplied by margins, quantities that are only 1–8% and 2–18%, respectively, of that supplied by rivers. However, 70–630 gigamoles per year of Fe could reach the ocean from margin sources—that is more than 23 times that supplied by dissolved river fluxes [*Jeandel et al.*, 2009].

Implications of Ocean Margins as a Source of Dissolved Elements

The mechanisms by which particles on ocean margins dissolve are not yet understood. It could involve organic substances, the formation of carbonate or Fe-Si coordination complexes on the particle surface; direct or indirect impact from bacterial activity; and/or the differential dissolution of minerals within the particle pool. For example, evidence of partial dissolution, with significant dissolved Si release, was observed in particulate matter–seawater batch experiments [*Jeandel et al.*, 2011].

Although margin sediment dissolution is probably incongruent along continental shelves, the fact that calculations show that these sediments are a significant source of elements and nutrients to the ocean highlights the need to properly quantify the processes yielding this new component of the land-to-ocean flux. For instance, if significantly higher inputs of Si than previously thought were reaching seawater, assuming steady state, models would reflect its reduced marine residence time, which would increase the calculated efficiency of the biological CO_2 pump. The additional flux of Mg could help balance the calculated Mg isotope budget of seawater, though the estimated additional source term from margins would require about a 12% increase in dolomite formation within the ocean, or an alternative and as yet undefined Mg sink [*Tipper et al.*, 2006].

Improving Climate Models

Revised Ca, Mg, Si, and Fe fluxes to seawater from submarine silicate weathering, in addition to the subaerial weathering [*Gaillardet et al.*, 1999] could provide important new constraints on the regulation of the atmospheric CO_2, and thus climate, on geological time scales. Importantly, this additional term is driven by the supply of material through physical erosion, further stressing the key role played by physical denudation in the delivery of dissolved elements to the ocean [*West et al.*, 2005]. More specifically, Si and Fe fluxes from margins may be significantly larger than those associated with dissolved river and atmospheric dust inputs alone, thus requiring a revised assessment of their role in regulating modern and past ocean primary productivity. As a whole, incorporating these additional fluxes in climate models could modify scientific understanding of how Earth's climate may evolve in the future.

An improved understanding of margin processes, particularly the release rates of various elements during oceanic sediment dissolution, is a priority of the international program GEOTRACES (http://www.geotraces.org). Experimental and field studies need to be conducted to determine dissolution kinetics and fluxes of Si, Ca, Mg, Sr, Fe, REE, and other tracers. Development of coupled ocean-continent models at regional and global scales as well as an improved characterization of sources, sinks, and transformations of elements and their isotopes will also contribute to a better understanding of the mechanisms that influence the present climate. Such efforts are prerequisites to improving reconstructions and predictions of land-to-ocean input variations and climate evolution.

Acknowledgments

The authors are grateful to Derek Vance, Bruno Hamelin, and Jacques Schott for their constructive discussions on this topic. Comments from Albert Galy, Anny Cazenave, and an anonymous reviewer helped to improve this article. We acknowledge funding from Centre National de la Recherche Scientifique poste rouge for Bernhard Peucker-Ehrenbrink.

References

Arsouze, T., J.-C. Dutay, F. Lacan, and C. Jeandel (2009), Reconstructing the Nd oceanic cycle using a coupled dynamical–biogeochemical model, Biogeosciences, 6(3), 5549–5588, doi:10.5194/bgd-6-5549-2009.

Berner, E. K., and R. A. Berner (1996), Global Environment: Water, Air, and Geochemical Cycles, 376 pp., Prentice Hall, Upper Saddle River, N. J.

Elrod, V. A., W. M. Berelson, K. H. Coale, and K. S. Johnson (2004), The flux of iron from continental shelf sediments: A missing source for global budgets, Geophys. Res. Lett., 31, L12307, doi:10.1029/2004GL020216.

Fripiat, F., A.-J. Cavagna, L. André, N. Savoye, F. Dehairs, and D. Cardinal (2011), Isotopic constraints on the Si-biogeochemical cycle of the Antarctic Zone in the Kerguelen area (KEOPS), Mar. Chem., 123(1-4), 11–22, doi:10.1016/j.marchem.2010.08.005.

Gaillardet, J., B. Dupré, and C. J. Allègre (1999), Geochemistry of large river suspended sediments: Silicate weathering or recycling tracer?, Geochim. Cosmochim. Acta, 63(23-24), 4037–4051, doi:10.1016/S0016-7037(99)00307-5.

Gislason, S. R., et al. (2008), Direct evidence of the feedback between climate and weathering, Earth Planet. Sci. Lett., 277(1-2), 213–222, doi:10.1016/j.epsl.2008.10.018.

Jeandel, C., Y. Godderis, B. Peucker-Ehrenbrink, F. Lacan, and T. Arsouze (2009), Impact of ocean margin processes on dissolved Si, Ca and Mg inputs to the ocean, Geochim. Cosmochim. Acta, 73(13), suppl. S, A588–A588.

Jeandel, C., C. Pradoux, Y. Zhang, P. van Beek, F. Lacan, M. Jones, and C. Pierce (2011), Land-to-ocean processes on and along the Kerguelen plateau traced by the REE concentrations and Nd isotopic composition, paper presented at 43rd International Liège Colloquium on Ocean Dynamics: Traces and Tracers, Univ. of Liege, Liege, Belgium, 2–6 May.

Jickells, T. D., et al. (2005), Global iron connections between desert dust, ocean biogeochemistry and climate, Science, 308(5718), 67–71, doi:10.1126/science.1105959.

Lacan, F., and C. Jeandel (2005), Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent–ocean interface, Earth Planet. Sci. Lett., 232(3-4), 245–257, doi:10.1016/j.epsl.2005.01.004.

Moore, J. K., and O. Braucher (2008), Sedimentary and mineral dust sources of dissolved iron to the world ocean, *Biogeosciences, 5*(3), 631–656, doi:10.5194/bg-5-631-2008.

Oelkers, E. H., S. R. Gislason, E. S. Eiriksdottir, M. Jones, C. R. Pearce, and C. Jeandel (2011), The role of riverine particulate material on the

global cycles of the elements, *Appl. Geochem., 26*, suppl. 1, S365–S369, doi:10.1016/j.apgeochem.2011.03.062.
Peucker-Ehrenbrink, B. (2009), Land2Sea database of river drainage basin sizes, annual water discharges, and suspended sediment fluxes, *Geochem. Geophys. Geosyst., 10*, Q06014, doi:10.1029/2008GC002356.
Peucker-Ehrenbrink, B., M. W. Miller, T. Arsouze, and C. Jeandel (2010), Continental bedrock and riverine fluxes of strontium and neodymium isotopes to the oceans, *Geochem. Geophys. Geosyst., 11*, Q03016, doi:10.1029/2009GC002869.
Radic, A., F. Lacan, and J. Murray (2011), Isotopic composition of dissolved iron in the Equatorial Pacific Ocean: Constraints for the oceanic iron cycle, *Earth Planet. Sci. Lett.*, in press.
Severmann, S., J. McManus, W. M. Berelson, and D. E. Hammond (2010), The continental shelf benthic iron flux and its isotope composition, *Geochim. Cosmochim. Acta, 74*(14), 3984–4004, doi:10.1016/j.gca.2010.04.022.
Sholkovitz, E., and R. Szymczak (2000), The estuarine chemistry of rare earth elements: Comparison of the Amazon, Fly, Sepik and the Gulf of Papua systems, *Earth Planet. Sci. Lett., 179*(2), 299–309, doi:10.1016/S0012-821X(00)00112-6.
Tagliabue, A., et al. (2010), Hydrothermal iron contribution to oceanic dissolved iron inventory, *Nat. Geosci., 3*, 252–256, doi:10.1038/NGEO818.
Thullner, M., A. W. Dale, and P. Regnier (2010), Correction to "Global-scale quantification of mineralization pathways in marine sediments: A reaction-transport modeling approach," *Geochem. Geophys. Geosyst., 11*, Q12002, doi:10.1029/2010GC003409.
Tipper, E. T., A. Galy, and M. J. Bickle (2006), Riverine evidence for a fractionated reservoir of Ca and Mg on the continents: Implications for the oceanic Ca cycle, *Earth Planet. Sci. Lett., 247*(3-4), 267–279, doi:10.1016/j.epsl.2006.04.033.
West, A. J., A. Galy, and M. Bickle (2005), Tectonic and climatic controls on silicate weathering, *Earth Planet. Sci. Lett., 235*(1-2), 211–228, doi:10.1016/j.epsl.2005.03.020.

Author Information

Catherine Jeandel, Laboratoire d'Etudes en Géophysique et Océanographie Spatiale (LEGOS), Centre National de la Recherche Scientifique (CNRS)/Institut de Recherche pour le Développement (IRD)/Centre National d'Etudes Spaciales (CNES)/Université Paul Sabatier, Toulouse, France; E-mail: catherine.jeandel@legos.obs-mip.fr; Bernhard Peucker-Ehrenbrink, LEGOS, CNRS/IRD/CNES/Université Paul Sabatier; also at Woods Hole Oceanographic Institution, Woods Hole, Mass.; Morgan T. Jones, Institute of Earth Science, University of Iceland, Reykjavik, Iceland; Christopher R. Pearce, Department of Earth and Environmental Sciences, Open University, Milton Keynes, UK; Eric H. Oelkers and Yves Godderis, Geosciences Environnement Toulouse, CNRS/IRD/Université Paul Sabatier, Observatoire Midi-Pyrénées, Toulouse, France; François Lacan, LEGOS, CNRS/IRD/CNES/Université Paul Sabatier; Olivier Aumont, Laboratoire de Physique des Océans, Plouzané, France; and Thomas Arsouze, Lamont-Doherty Earth Observatory, Palisades, N. Y.

NEWS

Mission Provides New Findings About Mercury

PAGES 218–219

Mercury once was considered by even some planetary scientists as "an example, to use a phrase coined by a very famous scientist, as 'one of the burnt-out cinders of the solar system.' And it is anything but that," Sean Solomon, who is principal investigator of NASA's Mercury Surface, Space Environment, Geochemistry and Ranging (MESSENGER) spacecraft, said at a 16 June briefing at NASA headquarters in Washington, D. C. Scientists at the briefing announced significant new findings about the planet's chemical composition, topography, magnetic field, and other features.

MESSENGER has now logged more than 1 Mercurian year (about 88 Earth days) as the first satellite in orbit around the closest planet to the Sun, and new understandings are being gleaned from the spacecraft's imaging system, which has already taken more than 20,000 images of Mercury. In addition, the laser altimeter has operated more than 2 million times from orbit thus far, and other instruments are also gathering extensive data about the planet.

Orbital images, which are currently filling in coverage of Mercury's northern polar region, show a number of broad planetary features, including vast expanses of smooth plains near the north pole that are thought to be volcanic in origin. These could have implications regarding the evolution of Mercury's crust and how it was formed, according to Brett Denevi, staff scientist with the Johns Hopkins University Applied Physics Laboratory (APL), Laurel, Md., which manages and operates the MESSENGER mission for NASA. In addition, the mission is collecting high-resolution imagery of specific features including some impact craters, examples of impact melt, and clusters of rimless irregular pits. "In less than 3 months, we have filled in a great deal of the planet already, at least for this [northern] hemisphere," Denevi said.

The laser altimeter—which sends short pulses from a powerful laser to the surface 8 times per second—is providing a much better understanding of the topography of the planet's surface. "We're seeing the broad shape of the planet for the first time," while also seeing detailed profiles of many geological features, according to Solomon, director of the Department of Terrestrial Magnetism (DTM) at the Carnegie Institution of Washington and a past president of AGU.

He said one investigation using altimetry is pursuing a decades-old mystery about whether some features—which appear to be bright deposits at radar wavelengths in a radar image of the northern polar region obtained from the Arecibo Observatory in Puerto Rico—might be water ice residing on the floors of impact craters in permanent shadow that remain cold. In a first analysis, with altimetry from a 25-kilometer wide crater combined with calculations of where the Sun shines on Mercury's surface, "this crater passes the test," said Solomon. He noted that the portion of the crater floor in permanent shadow coincides with the portion of the floor where radar bright deposits have been hypothesized to be water ice, and that other results—including from geochemical remote sensing instruments—would provide further information.

"If water is the major constituent of the polar deposits on Mercury, then we have the irony that the planet closest to the Sun is going to have more ice on its pole than even our own moon. Stay tuned," said Solomon.

Regarding Mercury's internal magnetic field, measurements indicate that the planet's magnetic equator is located 0.2 Mercury radii (about 480 kilometers) north of the geographical equator. Referring to Mercury's north and south poles, where the magnetic field lines do not close around the planet, Solomon said open field lines "are like interstate highways for charged particles from the interplanetary environment," which can kick off material from the surface and contribute to the planet's exosphere among other things.

Ralph McNutt Jr., mission project scientist with APL, noted at the briefing that although the Mariner 10 spacecraft had discovered major bursts of energetic particles in Mercury's magnetosphere during its flybys of the planet in 1974, MESSENGER's energetic particle spectrometer had been silent during its flybys. However, he said that since the spacecraft's insertion into orbit, bursts of energetic electrons have been observed during most orbits.

The spacecraft's X-Ray Spectrometer (XRS) has been providing new findings about some elemental ratios. Larry Nittler, staff scientist with DTM, said Mercury "has got lower aluminum and more magnesium relative to silicates, so it has a lower abundance of feldspar, and it clearly has undergone a unique geological history." He added that the XRS has found relatively low abundances of iron and titanium on Mercury's surface and a relatively high abundance of sulfur. Nittler said that the latter almost certainly relates to the planet's origin, "that Mercury most likely formed from building blocks that were fundamentally chemically different from those that formed the Earth and Moon originally."

Data from the gamma ray and neutron spectrometer show that Mercury has a higher than expected ratio of potassium to thorium, which according to Nittler indicates