THE GEOLOGICAL SOCIETY OF AMERICA®

RESEARCH FOCUS

Silicate weathering, volcanic degassing, and the climate tug of war

Matthew R. Saltzman
School of Earth Sciences, The Ohio State University, Columbus, Ohio 43210, USA

Long-term climate change is controlled primarily by the balance between CO_2 sources from volcanic and metamorphic degassing and by sinks tied to both silicate weathering and, to a lesser extent, organic carbon burial. Whereas a recent paper by McKenzie et al. (2016) argues that continental arc volcanism is the principal driver of greenhouse-icehouse transitions over the past ~720 m.y., in this issue of *Geology*, Swanson-Hysell and Macdonald (2017) bolster the idea that cooling and ice buildup can be driven by changes in silicate weathering, provided that the right rock (calcium-rich, mafic arc) is uplifted in the right place (warm, wet tropics). Each side of the source-sink coin is associated with imperfect geologic proxies. In the case of the degassing flux, detrital zircon geochronology may potentially reveal variations through time; low sedimentary proportions of young zircons, which form in melts concentrated along continental subduction zones, suggest low CO_2 fluxes (Lee et al., 2015; McKenzie et al., 2016). For silicate weathering, radiogenic isotopes studies (e.g., Sr, Nd, Li) of sedimentary successions provide information on changes in the age or composition of source rocks undergoing weathering (probably yielding only limited information about rates of weathering) (Kump and Arthur, 1997; Bataille et al., 2017). As with most geochemical proxies, each individual radiogenic isotope curve is of limited value on its own but gains interpretive strength when combined with others.

It is generally agreed upon that there are three greenhouse-icehouse transitions in the Phanerozoic (Paleogene, Late Paleozoic, and end-Ordovician). For the Paleogene, it was proposed (Raymo et al., 1988) that the Himalayan uplift affected CO_2 sinks through enhanced silicate weathering interpreted in part from a prominent increase in seawater $^{87}Sr/^{86}Sr$, although disentangling the role of carbonate weathering remains a vexing problem (Jacobson et al., 2002). Furthermore, constraints imposed by carbon-cycle mass balance require that if silicate weathering rates did increase locally in uplifted regions of the Himalaya, this must be quickly (over time scales greater than ~10,000 years) balanced out by a decrease in silicate weathering elsewhere on Earth's surface, such that net global weathering rates effectively match degassing (Kump and Arthur, 1997). If CO_2 degassing and silicate weathering were not in balance on these time scales, excessively large fluctuations could lead to a complete loss of atmospheric CO_2 on Earth. More recent Cenozoic studies have examined both the role of declining degassing (Mills et al., 2014), perhaps associated with reduction in continental arc volcanism (McKenzie et al., 2016), and arc weathering in the tropics (Jagoutz et al., 2016). The Late Paleozoic greenhouse-icehouse transition has been attributed to a lowering of atmospheric CO_2 levels brought about, in part, by the rise of land plants and their effect on silicate weathering and organic carbon burial (Berner, 2004), although this issue is far from settled (Montañez and Poulsen, 2013).

Arguably the most problematic icehouse transition has always been the Hirnantian (end-Ordovician) glaciation, which appears as a relatively short-lived cooling within a strong greenhouse interval. As such, it has been difficult for models to get CO_2 levels low enough to make ice (Berner, 2004). Everything "under the sun" has been proposed: Brenchley et al. (1994) emphasized organic carbon burial, Kump et al. (1999) and Young et al. (2009) drew attention to Late Ordovician tectonic uplift and silicate weathering in relation to degassing, Nardin et al. (2011) pointed to paleogeography and continental positioning, Lenton et al. (2012) discussed the role of early plants on silicate weathering and organic carbon burial, and Herrmann et al. (2004) and Pohl et al. (2016) addressed the importance of thresholds in pCO_2 in relation to ocean circulation and sea level. The list goes on. Rigorous testing of these hypotheses has limitations though; how well do we really know when the cooling and ice buildup began (e.g., Pope and Steffen, 2003; Saltzman and Young, 2005; Rasmussen et al., 2016)? The Swanson-Hysell and Macdonald paper won't end the debate over the Ordovician icehouse transition, but it does bring into focus the critical role that regional tectonics, paleogeography, and continental arc weathering must have played.

A struggle that anyone who works on the long-term carbon cycle has faced is bridging the gap between the evidence for changes in Earth's climate (studied by sedimentary geologists) and the direct evidence for the tectonic changes that produce them (structural, igneous, and metamorphic geology). Swanson-Hysell and Macdonald show us the fruits of an integrated study that links these generally distinct sets of literature, in their case involving paleomagnetic evidence for the latitudinal positioning of Ordovician volcanic source rocks (their figure 1) and geochemical study of coeval sedimentary rocks (their figure 2). In large part, their paper is a synthesis of existing data, which allows for the most holistic view to date of the problems posed by the Ordovician icehouse transition. Previous studies have recognized the importance of coupled strontium ($^{87}Sr/^{86}Sr$) and neodymium (ε_{Nd}) isotope stratigraphy, which can simultaneously address changes in global and local silicate weathering, but Swanson-Hysell and Macdonald are the first to showcase this approach for the Ordovician in their groundbreaking paper that complements the recent Neoproterozoic efforts of Cox et al. (2016).

The Ordovician convergence of the Iapetus ocean resulted in arc volcanism along the Laurentian continental margin (e.g., van Staal and Hatcher, 2010), but linking the weathering of these arc volcanics (i.e., Bronson Hill, Notre Dame, and Popelogan-Victoria arcs) to global climate is the challenge taken up by Swanson-Hysell and Macdonald. Young et al. (2009), building on the ideas of Kump et al. (1999) and Shields et al. (2003), examined the role of arc volcanic weathering based on a rapid decrease in the global seawater $^{87}Sr/^{86}Sr$ (see also Berner, 2006) and noted that ε_{Nd} changes were consistent with an Appalachian (Taconic) weathering signature (Gleason et al., 2002; Wright et al., 2002). However, the question of whether the latitudinal distribution of the Taconic arc volcanics was appropriately warm and wet, and demonstration of expected leads and lags in $^{87}Sr/^{86}Sr$ and ε_{Nd} trends, were not addressed by Young et al. (2009). Swanson-Hysell and Macdonald painstakingly demonstrate with paleomagnetic data that arc volcanics along the Appalachian margin were within the warm and wet tropics where chemical weathering rates are highest, and not the arid subtropics as previously published. Furthermore, they show that the onset of a prominent Ordovician $^{87}Sr/^{86}Sr$ seawater fall beginning at ca. 464 Ma, which occurs at a rate (0.0001/m.y.) that is among the steepest in the entire Phanerozoic (Saltzman et al., 2014), lags the ε_{Nd} shift in a manner predicted by much the shorter sediment source-to-sink transit time of Nd compared to the residence time of Sr in the oceans.

Like any innovative paper, Swanson-Hysell and Macdonald's work raises as many questions as it answers. Did the Taconic arc-continent

GEOLOGY, August 2017; v. 45; no. 8; p. 763–764 | doi:10.1130/focus082017.1

collision occur in the wet tropics as opposed to arid subtropics? Yes, and more generally this can explain why only some arc-continent collisions can drive icehouse transitions. Still, some caution is warranted in the actual proxy evidence for enhanced Taconic weathering, because while the ε_{Nd} increase demonstrates unequivocally that continental weathering shifted to younger source rocks at ca. 464 Ma in the Appalachian region (and later in more cratonal portions of Laurentia), an Ordovician arc volcanic end member is difficult to unambiguously detect using Nd isotopes in sediments which fall within the range of values expected for Grenville crust (Bock et al., 1998; Gleason et al., 2002). Similarly, because Swanson-Hysell and Macdonald rely on measurements of ε_{Nd} from clastic sediments (dated using U-Pb zircon ages) and $^{87}Sr/^{86}Sr$ from carbonate-dominated successions (relying on conodont biostratigraphy), they acknowledge that there is ambiguity in the proposed lead-lag relationship. Lastly, the existing Ordovician $\delta^{18}O$ paleotemperature curve is relatively poorly constrained in the interval of changing ε_{Nd} and $^{87}Sr/^{86}Sr$, leaving open questions about the extent to which theoretical cooling matches actual cooling. In order to be consistent with the paleotemperature curve of Trotter et al. (2008), Young et al. (2009) balanced enhanced weathering with increased degassing until the end of the Ordovician (mid-late Katian). Without more highly resolved constraints on the degassing flux and leads and lags in the isotope curves, a consensus view of the cause(s) of the Ordovician greenhouse-icehouse transition will likely remain elusive. Ultimately, integration of radiogenic isotope records with detrital zircon records may allow us to tap into the promise of studying the sedimentary and volcanic records in parallel throughout geologic history.

REFERENCES CITED

Berner, R.A., 2004, The Phanerozoic Carbon Cycle: CO_2 and O_2: Oxford, UK, Oxford University Press, 150 p.

Berner, R.A., 2006, Inclusion of the weathering of volcanic rocks in the GEOCARBSULF model: American Journal of Science, v. 306, p. 295–302, doi:10.2475/05.2006.01.

Bataille, C.P., Willis, A., Yang, X., and Liu, X.-M., 2017, Continental igneous rock composition: A major control of past global chemical weathering: Science Advances, v. 3, p. e1602183, doi:10.1126/sciadv.1602183.

Bock, B., McLennan, S.M., and Hanson, G.N., 1998, Geochemistry and provenance of the middle Ordovician Austin Glen member (Normanskill formation) and the Taconian orogeny in New England: Sedimentology, v. 45, p. 635–655, doi:10.1046/j.1365-3091.1998.00168.x.

Brenchley, P.J., Marshall, J.D., Carden, G.A.F., Robertson, D.B.R., Long, D.G.F., Meidla, T., Hints, L., and Anderson, T.F., 1994, Bathymetric and isotopic evidence for a short-lived Late Ordovician glaciation in a greenhouse period: Geology, v. 22, p. 295–298, doi:10.1130/0091-7613(1994)022<0295:BAIEFA>2.3.CO;2.

Cox, G.M., Halverson, G.P., Stevenson, R.K., Vokaty, M., Poirier, A., Kunzmann, M., Li, Z.-X., Denyszyn, S.W., Strauss, J.V., and Macdonald, F.A., 2016, Continental flood basalt weathering as a trigger for Neoproterozoic snowball earth: Earth and Planetary Science Letters, v. 446, p. 89–99, doi:10.1016/j.epsl.2016.04.016.

Gleason, J.D., Finney, S.C., and Gehrels, G.E., 2002, Paleotectonic implications of a Mid- to Late-Ordovician provenance shift, as recorded in sedimentary strata of the Ouachita and Southern Appalachian Mountains: The Journal of Geology, v. 110, p. 291–304, doi:10.1086/339533.

Herrmann, A.D., Haupt, B.J., Patzkowsky, M.E., Seidov, D., and Slingerland, R.L., 2004, Response of Late Ordovician paleoceanography to changes in sea level, continental drift, and atmospheric pCO_2: Potential causes for long-term cooling and glaciation: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 210, p. 385–401, doi:10.1016/j.palaeo.2004.02.034.

Jacobson, A.D., Blum, J.D., and Walter, L.M., 2002, Reconciling the elemental and Sr isotope composition of Himalayan weathering fluxes: Insights from the carbonate geochemistry of stream waters: Geochimica et Cosmochimica Acta, v. 66, p. 3417–3429, doi:10.1016/S0016-7037(02)00951-1.

Jagoutz, O., Macdonald, F.A., and Royden, L., 2016, Low-latitude arc–continent collision as a driver for global cooling: Proceedings of the National Academy of Sciences of the United States of America, v. 113, p. 4935–4940, doi:10.1073/pnas.1523667113.

Kump, L.R., and Arthur, M.A., 1997, Global chemical erosion during the Cenozoic: Weatherability balances the budgets, *in* Ruddiman, W.F., ed., Tectonic uplift and climate change: New York, Plenum Press, p. 399–426, doi:10.1007/978-1-4615-5935-1_18.

Kump, L.R., Arthur, M.A., Patzkowsky, M.E., Gibbs, M.T., Pinkus, D.S., and Sheehan, P.M., 1999, A weathering hypothesis for glaciation at high atmospheric pCO_2 during the Late Ordovician: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 152, p. 173–187, doi:10.1016/S0031-0182(99)00046-2.

Lee, C.-T.A., Thurner, S., Paterson, S., and Cao, W., 2015, The rise and fall of continental arcs: interplays between magmatism, uplift, weathering, and climate: Earth and Planetary Science Letters, v. 425, p. 105–119, doi:10.1016/j.epsl.2015.05.045.

Lenton, T.M., Crouch, M., Johnson, M., Pires, N., and Dolan, L., 2012, First plants cooled the Ordovician: Nature Geoscience, v. 5, p. 86–89, doi:10.1038/ngeo1390.

McKenzie, N.R., Horton, B.K., Loomis, S.E., Stockli, D.F., Planavsky, N.J., and Lee, C.-T.A., 2016, Continental arc volcanism as the principal driver of icehouse-greenhouse variability: Science, v. 352, p. 444–447, doi:10.1126/science.aad5787.

Mills, B., Daines, S.J., and Lenton, T.M., 2014, Changing tectonic controls on the long-term carbon cycle from Mesozoic to present: Geochemistry Geophysics Geosystems, v. 15, p. 4866–4884, doi:10.1002/2014GC005530.

Montañez, I.P., and Poulsen, C.J., 2013, The Late Paleozoic Ice Age: An Evolving Paradigm: Annual Review of Earth and Planetary Sciences, v. 41, p. 629–656, doi:10.1146/annurev.earth.031208.100118.

Nardin, E., Goddéris, Y., Donnadieu, Y., Le Hir, G., Blackey, R.C., Pucéat, E., and Aretz, M., 2011, Modeling the early Paleozoic long-term climatic trend: Geological Society of America Bulletin, v. 123, p. 1181–1192, doi:10.1130/B30364.1.

Pohl, A., Nardin, E., Vandenbroucke, T.R.A., and Donnadieu, Y., 2016, High dependence of Ordovician ocean surface circulation on atmospheric CO_2 levels: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 458, p. 39–51, doi:10.1016/j.palaeo.2015.09.036.

Pope, M.C., and Steffen, J.B., 2003, Widespread, prolonged late Middle to Late Ordovician upwelling in North America: A proxy record of glaciation?: Geology, v. 31, p. 63–66, doi:10.1130/0091-7613(2003)031<0063:WPLMTL>2.0.CO;2.

Rasmussen, C.M.Ø., et al., 2016, Onset of the main Phanerozoic marine radiation sparked by emerging Mid Ordovician icehouse: Nature Scientific Reports, v. 6, p. 18884, doi:10.1038/srep18884.

Raymo, M.E., Ruddiman, W.F., and Froelich, P.N., 1988, Influence of late Cenozoic mountain building on ocean geochemical cycles: Geology, v. 16, p. 649–653, doi:10.1130/0091-7613(1988)016<0649:IOLCMB>2.3.CO;2.

Saltzman, M.R., and Young, S.A., 2005, A long-lived glaciation in the Late Ordovician?: Isotopic and sequence stratigraphic evidence from western Laurentia: Geology, v. 33, p. 109–112, doi:10.1130/G21219.1.

Saltzman, M.R., Edwards, C.T., Leslie, S.A., Dwyer, G.S., Bauer, J.A., Repetski, J., Harris, A., and Bergström, S.M., 2014, Calibration of a conodont apatite-based Ordovician $^{87}Sr/^{86}Sr$ curve to biostratigraphy and geochronology: Implications for stratigraphic resolution: Geological Society of America Bulletin, v. 126, p. 1551–1568, doi:10.1130/B31038.1.

Shields, G.A., Carden, G.A., Veizer, J., Meidla, T., Rong, J., and Li, R., 2003, Sr, C, and O isotope geochemistry of Ordovician brachiopods: A major isotopic event around the Middle-Late Ordovician transition: Geochimica et Cosmochimica Acta, v. 67, p. 2005–2025, doi:10.1016/S0016-7037(02)01116-X.

Swanson-Hysell, N.L., and Macdonald, F.A., 2017, Tropical weathering of the Taconic orogeny as a driver for Ordovician cooling: Geology, v. 45, p. 719–722, doi:10.1130/G38985.1

Trotter, J.A., Williams, I.S., Barnes, C.R., Lécuyer, C., and Nicoll, R.S., 2008, Did cooling oceans trigger Ordovician biodiversification? Evidence from conodont thermometry: Science, v. 321, p. 550–554.

van Staal, C.R., and Hatcher, R.D., Jr., 2010, Global setting of Ordovician orogenesis, *in* Finney, S.C., and Berry W.B.N., eds., The Ordovician Earth System: Geological Society of America Special Papers, v. 466, p. 1–11, doi:10.1130/2010.2466(01).

Wright, C.A., Barnes, C.R., and Jacobsen, S.B., 2002, Neodymium isotopic composition of Ordovician conodonts as a seawater proxy: Testing paleogeography: Geochemistry Geophysics Geosystems, v. 3, doi:10.1029/2001GC000195.

Young, S.A., Saltzman, M.R., Foland, K., Linder, J., and Kump, L., 2009, A major drop in seawater $^{87}Sr/^{86}Sr$ during the Middle Ordovician (Darriwilian): Links to volcanism and climate?: Geology, v. 37, p. 951–954, doi:10.1130/G30152A.1.

Printed in USA