SUBARU OUTSTANDING WOMAN IN SCIENCE AWARD

Presented to Kateryna Klochko

Kateryna Klochko
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Citation by Alan Jay Kaufman

Public awareness of the consequence of the buildup of greenhouse gases on global climate and shallow ocean acidification puts pressure on geoscientists to construct viable records of CO_2 variations in the atmosphere and world ocean through ancient time. This is relatively simple for the last half million years or so where ice cores provide archives of atmospheric inventories; older records remain elusive but for the potential of reconstructing CO_2 concentrations and seawater pH through boron isotope measurements. Many paleoceanographers are racing to make these difficult isotopic measurements, but few at any level have stepped back to ponder the myriad of proxy assumptions.

One who has is the 2010 Subaru Outstanding Woman in Science recipient, Kateryna "Katya" Klochko — currently a Postdoctoral Associate at the Carnegie Institution for Science — who set out to test several of the poorly constrained assumptions of the critical boron isotope proxy for her dissertation research. Upon arriving at the University of Maryland in 2003, Katya initiated an ambitious project to develop a laser ablation ICP-MS technique for the boron isotope measurement of carbonate rocks as a potential seawater pH barometer. Development of a laser ablation technique on solid carbonate is considered important because boron is ubiquitous in surface environments, and is therefore a common contaminant in solution chemistry.

Although initial laser ablation experiments showed promise towards the analysis of a variety of natural carbonates, the interpretation of the boron isotope data and its use in the reconstruction of pH and CO_2 concentrations in past oceans nagged Katya who delved deeper into several critical assumptions associated with the pH proxy. This approach is characteristic of this focused scientist who assumes that nature is understandable and that she has the capacity to understand it. Furthermore, Klochko is constantly searching for deeper rather than superficial knowledge.

Among the assumptions used in the pH proxy include knowledge of the boron isotopic difference between the two main boron-bearing species in seawater (i.e. boric acid [$B(OH)_3$] and borate ion [$B(OH)^{4-}$]). Previously this was only known from ab initio calculations insofar as it is not currently possible to quantitatively separate these species from seawater in order to measure their isotope differences. After thinking about the problem for several months, Katya reached out to theoretical chemist Jack Tossell in the Chemistry Department who introduced her to Robert Byrne, an oceanographer at the University of South Florida. Byrne suggested that a spectrophotometric technique he developed at USF might be used to empirically measure the boron isotope differences, and invited Katya to come to his laboratory. The result was spectacular. Katya was able to make the novel measurements and found a much larger isotope contrast than what was previously assumed (see Byrne et al., 2006, in Deep Sea Research and Klochko et al., 2006, in Earth and Planetary Science Letters) and which has propagated through the literature for over 30 years. Katya's research thus has an immediate and profound impact on carbonate-based pH reconstructions of past oceans.

Building on this success Katya moved on to a second long-standing assumption of the carbonate pH proxy – that the charged borate ion is preferentially incorporated into carbonate minerals relative to the neutral boric acid species. Given their large boron isotopic differences, the relative proportion of each has a strong influence on the measured boron isotopic composition of the carbonate rock. To test this proxy assumption Klochko contacted George Cody at the Carnegie Institution for Science and initiated NMR studies of modern biogenic carbonates. Contrary to previous expectations, Katya's NMR measurements revealed almost equal proportions of charged borate and uncharged boric acid in both aragonite and calcite precipitates (see Klochko et al., 2009, in Geochimica et Cosmochimica Acta). This unexpected result further underscores the view that controls on boron isotope composition in marine carbonates, and hence the pH proxy, are more complex that previously suggested.

Finally, in her continued efforts to find novel tests of the pH proxy, Katya started a series of carefully designed pH-controlled carbonate precipitation experiments with post-doctoral fellow Sang-tae Kim in the stable isotope facility at the University of Maryland and Gavin Foster at the University of Bristol. She believes that the next step to a better understanding of the proxy will be to isolate and constrain mineralogical effects on boron speciation and isotope compositions. These bench top experiments are on-going now at the Carnegie Institution for Science (where she is currently investigating the interaction of small organic molecules with mineral surfaces in collaboration with Robert Hazen and Dimitri Sverjensky) but preliminary boron isotopic results from samples precipitated at

Maryland under high pH conditions confirm Katya's spectroscopic observations.

Katya's successful integrated efforts towards a unified scientific goal are exemplary. She reveals a willingness to explore new techniques and analytical tools, and has developed the people skills necessary to reach out to the large number of both senior and junior scientists involved in her research.

Matching her research abilities, Klochko has the great ability to convey difficult concepts to both general and professional audiences, which is all the more impressive given that English is not her first language. She works hard on her presentations, which have been recognized by fellow colleagues at three American Geophysical Union annual meetings and by the Geology Department faculty during our bi-annual graduate student presentation day. During her graduate years Katya won first and second place in the Ph.D. category for her carefully crafted talks. In addition, Klochko was awarded a graduate student fellowship of $1500 by the Geological Society of America in 2005, and her final semester at the University of Maryland was funded by an Ann G. Wylie Dissertation Fellowship.

Kateryna Klochko has a bright future ahead of her, and the paleoceanographic community has already benefited from her groundbreaking dissertation. Her publications have been referenced by several leaders in the field, including Elderfield, McCulloch, Lemarchand, Hemming, and Broecker. Klochko's "pH.D." dissertation is causing leading scientists to rethink their assumptions about this important proxy, and its implications for charting the pH of ancient oceans and pCO_2 of ancient atmospheres. In a recent mini-conference on boron isotopes at Columbia University, Katya's work was front and center; the fact that her studies are making waves in the oceanographic community is testament to the significance of her small but growing body of work.

Response by Kateryna Klochko

I am deeply honored to be chosen this year's recipient of the Subaru Outstanding Woman in Science Award in memory of Doris Curtis, the first female President of the society. I thank the GSA committee for this award and Subaru for its sponsorship.

I share this award with very special people whose enthusiastic support and mentorship made my research possible. These include my two academic advisors: Jay Kaufman and Jack Tossell at the University of Maryland, who nominated me for this award, Bob Byrne at the University of South Florida, who generously opened the doors of his busy laboratory for my equilibrium constant experiments, and George Cody at the Carnegie Institution of Washington for his keen interest and insight in my project, as well as his state-of-the-art NMR for my speciation experiments.

I thank the Geology Department at the University of Maryland with the outstanding geochemistry program, faculty and students.

Finally, I share this award with my dear mother Valentina Ninova, whose unconditional love and support guided me to where I stand today.