Noble gas isotope fractionation during air-sea exchange: A tracer for mechanisms that determine N_2/Ar ratios in the ocean

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Our observations indicate that the N_2/Ar ratio in the world's ocean increases from near equilibrium with the atmosphere at the surface to ~ 1.5 % supersaturation at depth (~ 1000 m) and the values in deep waters increase from the Atlantic to Pacific Ocean by ~ 0.5 %. The reason for the increase is a combination of air-sea exchange during formation of subsurface waters and denitrification below the euphotic zone. In order to separate these two processes one must understand bubble processes that occur during gas exchange. The change in gas ratios is more strongly influenced by small bubbles that totally collapse than larger bubbles that exchange gases across the bubble-water interface.

The isotope ratios of argon ($^{40}Ar/^{36}Ar$) and neon ($^{22}Ne/^{20}Ne$) are sensitive to the mechanisms of bubble processes because kinetic isotope fractionation caused by molecular diffusion coefficient differences is a tracer for the bubble exchange mechanism. We have determined the kinetic isotope fractionation factor during gas exchange for argon and neon in laboratory experiments to be – 3.3 ± 0.3 ‰ and – 6.7 ± 0.3 ‰ respectively. These values agree to within the estimated error of theoretical calculations [1] if one assumes the gas exchange process is proportional to the square root of the molecular diffusion coefficients. Using the measured fractionation factors in a gas exchange model [2] to determine the sensitivity of argon and neon isotope ratios to bubble processes suggests that neon isotopes might be a useful tracer for determining the importance of the bubble exchange mechanism. The changes, however, are small—on the order of 0.1-0.2 ‰ -- and to our knowledge, highly accurate neon isotope ratios in seawater are yet to be determined.

[1] Bourg & Sposito (2008) *Geochem. Cosmochim. Acta.* **72** 2237-2247. [2] *Stanley et al.* (2009) *Jour. Geophys. Res.* **114**, C11020, doi:1029/2009JC005396.

Rock alteration and element transfer during formation of U deposits related to Na-metasomatites in the Ukrainian Shield

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The Central Ukraine U Province is situated in the Ingul Megablock and along its eastern border in Kryvy Rig – Kremenchug syncline zone of the Ukrainian Shield. The Province includes about 20 U deposits and numerous U showings hosted by Palaeoproterozoic metamorphic and magmatic complexes. Two of these deposits (the Zhovta Richka and Pervomayske deposits) already have been exchaused but four U-deposits in the altered granitic rocks (Vatutynske, Novokostantynivka, Michurynske and Central deposits) are currently operated. Rock samples were selected in underground mines and from drillcores, were examined for mineral paragenesises using optical microscopy and after agate mortar crushing were analysed for major and trace elements with ICP-AES/-MS techniques (CNRS, Nancy, France). Element transfer was estimated using simply binary and/or isocon diagrams [1]. Multistaging of metasomatic alteration of the host rocks (dominantly granites and migmatites) provided sequential changing of mineral paragnesyses from earlier to later mineral paragenesises. The earliest alteration represents successive transformation of the host granitoids into chloritized granites and episyenites, which were progressively dequartzifized and eventually transformed into aegirine and aegirine-reibeckite albitites due to progressive K-Na exchange between hydrothermal solution and the rocks. Na, V, Ca and Sr were the most prominent extrinsic elements introducing in the host rocks during this stage of the alteration whereas Si, K and Rb were ejected. Next stage of hydrothermal activity provided carbonate metasomatism with partial leaching of the albitites and crystallization of garnet, epidote, calcite, magnetite and either Mg-amphyboles or phlogopite mineralization with reverse depletion in Na. Na, Si, V, Ba and P were transferred out of the albitite bodies but U, K, Rb, Ca, Sr, Mg, U, Mn, Zr, Hf and Co were added.

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