Protactinium-231 and Thorium-230 Abundances and High Scavenging Rates in the Western Arctic Ocean

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The Canadian Basin of the Arctic Ocean, largely ice covered and isolated from deep contact with the more dynamic Eurasian Basin by the Lomonosov Ridge, has historically been considered an area of low productivity and particle flux and sluggish circulation. High-sensitivity mass-spectrometric measurements of the naturally occurring radionuclides protactinium-231 and thorium-230 in the deep Canada Basin and on the adjacent shelf indicate high particle fluxes and scavenging rates in this region. The thorium-232 data suggest that offshore advection of particulate material from the shelves contributes to scavenging of reactive materials in areas of permanent ice cover.

Both ^{231}Pa [half-life ($t_{1/2}$) = 32,800 years] and ^{230}Th ($t_{1/2}$ = 75,400 years), which are produced at a constant ratio (24.5, atom/atom) throughout the oceans by the decay of ^{235}U and ^{234}U, respectively, are removed to sediments on a time scale of decades and are useful for investigating scavenging and sedimentation processes. Protactinium-231 has a longer residence time than ^{230}Th in seawater, ~100 compared with ~20 years, and thus is distributed to a larger extent by mixing and advection before removal (*1–4*). The finding of a general pattern of greater Pa removal at ocean margins and other areas of high particle flux inspired efforts to use sedimentary ^{230}Th/^{231}Pa records to reconstruct paleoproductivity (*5*). Studies have demonstrated that ventilation age (*4, 6, 7*) and particle composition (*8*) also affect the distribution and removal of these isotopes, complicating the interpretation of their modern and paleoceanographic distributions, yet offering the possibility of using them to study ventilation as well as scavenging processes.

The imprint of boundary scavenging on the distribution of ^{231}Pa and ^{230}Th may be pronounced in the Arctic Ocean because it has the greatest proportion of shelf area (~30%) of any ocean, and the shelves are seasonally ice free, whereas the deep basins are mostly perennially ice covered. The large resulting spatial and seasonal contrasts in productivity and particle flux in the Arctic affect geochemical cycling, including the removal of carbon to deep waters, the accumulation of particle-reactive species (including contaminants), and the export of these species to the Atlantic. The shelves are also sites of intermediate- and deep-water formation (*9, 10*), though data are scarce for the western Arctic (*11*). Before icebreaker expeditions, the Canada Basin was studied largely from isolated ice camps. Earlier studies of Th isotopes and ^{231}Pa in the open Arctic Ocean (*12–14*) have suggested that scavenging rates are extremely low in the western Arctic (Makarov and Canada basins) and higher, comparable to other oceans, in the Eurasian basins.

We collected unfiltered seawater samples in 1995 from two stations in the Beaufort Sea, one on the shelf, one in the ice-covered deep basin, aboard the icebreaker CCGS *Louis S. St. Laurent*. We used thermal ionization mass spectrometry (TIMS) to measure ^{230}Th, ^{232}Th (*7, 15*), and ^{231}Pa (^{231}Pa has not previously been measured by TIMS in seawater) (*16*). For all three isotopes, TIMS offers significant improvement in sample size (100- to 1000-fold), measurement precision (roughly 5 to 10% versus 20 to 40%), and measurement time (hours versus weeks) over radiochemical (alpha-counting) techniques.

The ^{230}Th and ^{231}Pa concentrations at the deep station (Fig. 1) increase nearly linearly with depth. This is typical of ^{230}Th profiles and is predicted by one-dimensional reversible exchange models (*17, 18*). In contrast, the few studies of water column ^{231}Pa have shown that concentrations typically are near constant below 1000 m (*6, 8, 12, 14, 19*). This has been attributed to the long scavenging residence time of ^{231}Pa, allowing horizontal redistribution. Our data show that this is not the case in the western Arctic, and that vertical (scavenging) processes dominate here. The average ^{230}Th and ^{231}Pa residence times calculated for the deep waters (>900 m) at station AO1 are 17 and 110 years, respectively, similar to other ocean basins.

These data contrast sharply with the only other ^{230}Th and ^{231}Pa profiles from the Canada Basin, at the CESAR Ice Station on the Alpha Ridge (*12*). At CESAR, where the water depth was 1600 m, total ^{230}Th concentrations were >20 fg per kilogram of seawater at 1500 m, almost four times as high as at station AO1, and the average deep-water Th residence time was ~40 years, consistent with the hypothesis that there is very little particle flux in the ice-covered Arctic. Concentrations of ^{231}Pa at CESAR were more than twice those found at similar depths at Station AO1. A clue to these differences may be found in the ^{232}Th data.

Thorium-232 ($t_{1/2}$ = 1.4 × 10^{10} years) is delivered to the oceans from the continents largely in riverine and air-borne particles (*20, 21*), and its concentration accordingly decreases from the shelf offshore and from surface to deep waters (Fig. 1). Although station AO1 is located in an area of permanent ice cover, as was the CESAR station, surface-water ^{232}Th concentrations (180 to 200 pg/kg) are much higher than those at

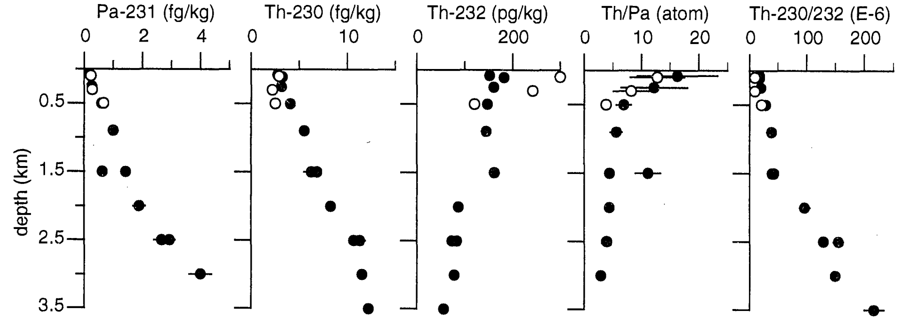

Fig. 1. Vertical profiles of total (dissolved plus particulate) ^{231}Pa, ^{230}Th, and ^{232}Th, measured by TIMS, and the ratios ^{230}Th/^{231}Pa and ^{230}Th/^{232}Th, at stations AO1 (72°32.5′N, 143°49.8′W, 3500 m) and AM10 (70°28.7′N, 136°55.8′W, 770 m) in the Canada Basin (*16*). Error bars (2σ) represent the maximum of counting statistics or run statistics, and are generally smaller than the symbols. A table of the isotope data is available at www.sciencemag.org/feature/data/976851.shl.

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the Alpha Ridge [<100 pg/kg (*12*)]. In addition, the ^{230}Th/^{232}Th ratios in the surface waters are only slightly higher than typical crustal values (*22*), suggesting that much of the ^{230}Th as well as ^{232}Th in the upper waters is detrital in origin. The temperature and salinity structure in the upper water column at station AO1 is identical to that at station AM10, consistent with rapid communication of these waters. Shelf particulate material advected offshore may therefore enhance scavenging rates and reactive element fluxes hundreds of kilometers from the ice edge.

Aside from the surface water data, the ^{230}Th and ^{231}Pa data at station AO1 are fit well by a scavenging model (*17, 18*) with particle concentrations and settling rates typical of other ocean basins (Fig. 2). The good fit of this model is consistent with the suggestion that vertical scavenging is the dominant process affecting both ^{230}Th and ^{231}Pa at station AO1, and that it is as efficient in this area of the Canada Basin as in most of the world's oceans. Incorporating ventilation along with scavenging (*6*) has only a small effect on the model profiles, because radiocarbon-based estimates for the age of Canada Basin Deep Water (CBDW) (*23, 24*) are 5 and 25 times the scavenging residence times of Pa and Th, respectively. Although our ^{230}Th and ^{231}Pa data are consistent with this age, the similarity between model profiles for scavenging alone and scavenging with mixing on this time scale means that the ^{230}Th and ^{231}Pa data cannot be used to constrain the age of CBDW.

Despite the consistency of the model Pa profiles with slow ventilation of CBDW, our finding of a linear ^{231}Pa profile at station AO1 is puzzling. In the North Pacific, where deep waters are even older and the basin wider, horizontal mixing allows exchange of deep waters with waters at the margins on a time scale comparable to the scavenging residence time of Pa (*25*), and ^{231}Pa concentrations below 1000 m level off or decrease with depth (*19*). Thus, the observations at station AO1 may indicate that horizontal mixing as well as ventilation is slow in the deep Canada Basin. This may bolster the suggestion of Macdonald and Carmack (*24*) that CBDW is a relict, stagnant water mass last ventilated ~500 years ago, rather than a water mass that is continually, albeit slowly, renewed (*23*). Above the CBDW, both the curvature of the CESAR profiles (*12*) and the suggestion of a change in slope of the AO1 profiles at ~1500 m (Fig. 1), near the sill depth of the Lomonosov Ridge, indicate that mixing is more rapid in intermediate waters.

Finally, although the differences in ^{230}Th and ^{231}Pa concentrations in the southern Beaufort Sea and at the Alpha Ridge demonstrate that there are wide variations in scavenging intensity in the Canada Basin as well as between the Canada and Eurasian basins, water column ^{230}Th/^{231}Pa ratios at these stations provide no evidence for large-scale fractionation of the two nuclides in the Arctic [see also (*14*)]. Recent work has demonstrated that particle composition plays a key role in the large-scale oceanic fractionation of Th and Pa (*8*). If this is the case, and a primary source of particles to the interior Arctic basins is by advection from the shelves, as indicated by the ^{232}Th data, fractionation of Th and Pa might be less than hypothesized from the variation in particle fluxes alone.

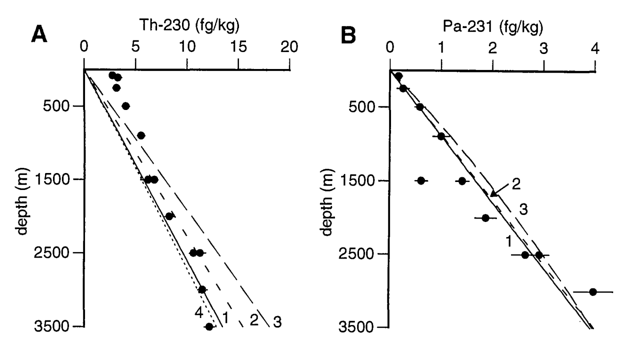

Fig. 2. Model curves for total ^{230}Th (**A**) and ^{231}Pa (**B**) in the deep Canada Basin based on scavenging alone (models 1 and 2) and scavenging plus ventilation (models 3 and 4), shown with the ^{230}Th and ^{231}Pa data from station AO1. Models 1 and 2 are based on the reversible exchange model (*17, 18, 28*), in which the adjustable parameters are the average settling rate of particulate material (*S*) and the concentration of suspended particulate material (*SPM*). For model curve 1, values of S = 1000 m/year and SPM = 10 μg/liter were used, whereas in model 2, the values used were S = 500 m/year and SPM = 20 μg/liter. The solid/solution partition coefficients (K_d's) used were 1.7×10^7 ml/g for Th and 2×10^6 ml/g for Pa. Model curves 3 and 4 are based on a mixing-scavenging model (*6*), in which the adjusted parameters are τ_w, the water renewal time, and τ_s, the scavenging residence time of Th or Pa. For simplicity, it is assumed that the entire water column is renewed with the same water mass at the same rate, in this case shelf water (the concentrations chosen were the average concentrations observed at station AM10), with a water renewal time of 500 years (*23, 24*). For model curve 3, the average Th and Pa residence times as determined from the AO1 data below 900 m were used for τ_s: 17 and 110 years, respectively. For model curve 4, a shorter τ_s for Th of 12 years, which is on the lower end of those determined from the data, was used. The poor match between the curves and the surface water Th data results in part from the absence in the models of vertical mixing and of rapid lateral advection of upper waters between the shelves and basin. The importance of the latter is apparent from the ^{232}Th data.

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16. We collected 1-liter samples of unfiltered seawater in acid-cleaned high density polyethylene bottles and stored them double-bagged until processing. All subsequent sample handling and chemical procedures were performed in a clean laboratory, with ultrapure reagents. Procedures for Th are modifications of those of R. L. Edwards, J. H. Chen, and G. J. Wasserburg [*Earth Planet. Sci. Lett.* **81**, 175 (1987)] and procedures for Pa are modifications of those of D. A. Pickett, M. T. Murrell, and R. W. Williams [*Anal. Chem.* **66**, 1044 (1994)]. Samples were acidified with HNO_3 and spiked with ^{229}Th and ^{233}Pa tracers and an Fe carrier. The amount of ^{233}Pa spike ($t_{1/2}$ = 27 days) was chosen to give ^{233}Pa/^{231}Pa ratios between 1 and 10. At this level the total amount of ^{233}Pa used (~10^8 atoms) did not substantially increase the darknoise of the detector. After letting the sample and spike equilibrate for 2 to 3 days with gentle heating, we coprecipitated Th and Pa with $Fe(OH)_3$ and purified them by anion exchange (*7, 26, 27*). The Th and Pa fractions were loaded onto zone-refined Re filaments (previously checked for contamination in the 229 to 233 mass range) in dilute nitric acid and covered with colloidal graphite. Because the Pa beams were small (<10 cps), 50 to 100 pg of ^{232}Th was added to the Pa fraction after chemical separation to aid in focusing the ion beam on the mass spectrometer. Measurements were made with a Finnigan MAT 262 RPQ mass spectrometer in ion-counting mode. Data reduction was done off-line, and corrections were made for darknoise, abundance sensitivity, spike isotopic compositions, blanks, and the evolution of the ^{233}Pa spike through time. Blank corrections, determined from two measurements for ^{231}Pa and ^{232}Th and three for ^{230}Th, amounted to 0.07 ± 0.07 fg for ^{231}Pa (1 to 13% of sample ^{231}Pa measured), 0.5 ± 0.3 fg for ^{230}Th (5 to 19%), and 6.5 ± 2.0 pg for ^{232}Th (2 to 10%). Duplicate samples were collected from 1500 and 2500 m at station AO1, and with the exception of the ^{231}Pa analyses at 1500 m, the results were reproducible. The cause of the anomalously low ^{231}Pa measurement has not been determined. Protactinium concentrations were not determined in two of the samples at Station AO1 (110 m and 3500 m) because the filament burned out before sufficient data could be collected.

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Is GRO J1744-28 a Strange Star?

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The unusual hard x-ray burster GRO J1744-28 recently discovered by the Compton Gamma-Ray Observatory can be modeled as a strange star with a dipolar magnetic field of $\leq 10^{11}$ gauss. According to this model, when the accreted mass of the star exceeds some critical mass, its crust breaks, resulting in the conversion of the accreted matter into strange matter and a release of energy. Subsequently, a fireball forms and expands relativistically outward. The expanding fireball interacts with the surrounding interstellar medium, causing its kinetic energy to be radiated in shock waves and producing a burst of x-ray radiation. The burst energy, duration, interval, and spectrum derived from such a model are consistent with the observations of GRO J1744-28.

GRO J1744-28 is a previously unknown type of x-ray transient source that was discovered on 2 December 1995 by the Burst and Transient Source Experiment (BATSE) on the Compton Gamma-Ray Observatory (GRO) (*1*). The bursts were detected up to energies of ~75 keV with intervals between bursts of ~200 s initially. After 2 days, the burst rate dropped to ~1 per hour (*2*). However, by 15 January 1996 the burst rate had increased to ~40 per day. The burst durations were ~10 s. The burst fluences (25 to 60 keV) ranged from 1.7×10^{-7} to 6.8×10^{-7} ergs cm^{-2}; the average fluence $\overline{S} = 2.7 (\pm 0.9) \times 10^{-7}$ ergs cm^{-2}. The position of the source is near the galactic center. For a distance of ~7.5 kpc, the average peak luminosity was $\sim 2 \times 10^{38}$ ergs s^{-1}, with a flux of $\sim 3 \times 10^{-8}$ergs cm^{-2} s^{-1}.

Analysis of the BATSE data indicated that the source is a binary pulsar with a pulsation period of 0.467 s, a companion with a mass of 0.22 to 1.0 $M_\odot$ (where $M_\odot$ is the mass of the sun) and a binary orbital period of 11.8 days (*3*). Because the x-ray mass function is small ($\sim 1.31 \times 10^{-4}\ M_\odot$), the system must be nearly face-on to an observer from Earth, with an inclination angle of ~18° (*3–5*). Furthermore, for the measured rotation period derivative to be consistent with standard accretion torque theory (*6*), the persistent luminosity of the source at its peak should be close to the Eddington limit (*4*) and the surface dipole magnetic field of the pulsar should be $\leq 10^{11}$ G (*3–5*). From the observed pulsed fraction and the pulsar's x-ray spectrum, the strength of the local surface magnetic field is estimated to be several teragauss (*4*). In addition, the proportional counter array (PCA) experiment (2 to 60 keV) on the Rossi X-ray Timing Explorer (RXTE) (*7*) had detected GRO J1744-28 during the period 18 January to 10 May 1996. The observations showed that after the earlier large bursts, the flux dipped below the preburst level by as much as 25 to 30% and then made a slow quasi-exponential recovery back toward the preburst level. The observed recovery period lasted up to ~1000 s for some bursts, but most bursts recovered in a few hundred seconds.

The properties of the hard x-ray bursts (HXRBs) from GRO J1744-28 differ from those of other known high-energy bursts—x-ray bursts, soft γ-ray bursts, and γ-ray bursts. First, the HXRBs are probably not type I x-ray bursts (*8*). Thus, thermonuclear flashes in matter accreted onto the surface of a neutron star may not produce HXRBs. Second, the durations of the HXRBs are several hundred times those of the three soft γ-ray repeaters, even though these two kinds of bursts have similar repeat times and spectra. Third, the HXRBs are different from γ-ray bursts, because γ-ray bursts do not have fast repeat times and their spectra are much harder. On the other hand, the repeat times and spectra of the HXRBs are somewhat similar to those of type II x-ray bursts from the rapid burster (*2*, *8*). This suggests that some accretion instability may be a mechanism for producing HXRBs. Cannizzo (*9*) studied the global, time-dependent evolution of the Lightman-Eardley instability, which might account for some observational features of the HXRBs. Here, we propose an alternative model in which a strange star accretes matter from its low-mass companion.

Strange matter (bulk quark matter) is conjectured to be more stable than hadronic matter (*10*). The existence of strange matter is allowable within uncertainties inherent in a strong-interaction calculation (*11*); thus, strange stars may exist in the universe. Strange stars have crusts with masses of $\sim 10^{-5} M_\odot$ (*12*). However, the postglitch behavior of pulsars can be described by the neutron-superfluid vortex creep theory (*13*), which requires a crustal mass of $\geq 10^{-3} M_\odot$. The conversion of a neutron star to a strange star may require the formation of a strange matter seed, which is produced through the deconfinement of neutron matter at a density of ~7 to 9 ρ_0 (where ρ_0 is the nuclear matter density), much larger than the central density of a 1.4$M_\odot$ neutron star with a moderately stiff to stiff equation of state (*14*). These two features suggest that strange stars may be formed in low-mass x-ray binaries (*15*) because when the neutron star in a low-mass x-ray binary accretes sufficient mass (perhaps $\geq 0.4 M_\odot$), its central density can reach the deconfinement density and the whole star will then undergo a phase transition to become a strange star. The phase transition from nuclear matter to strange matter under the condition of conserved charge rather than constant pressure may occur at a density as low as 2 to 3 ρ_0 (*16*). If so, strange stars may be formed during the evolution of protoneutron stars (*17*). Some arguments against the existence of strange stars should be kept in mind; for example, the disruption of a single strange star may contaminate the entire galaxy, and

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