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Aluminum-26 in Deep-Sea Sediment

Abstract. *The activity of ^{26}Al in a North Pacific core was found to be 0.081 ± 0.046 disintegration per minute per kilogram of dry sediment, which corresponds to a $^{26}Al/^{10}Be$ ratio of 0.018 ± 0.011 (or 0.019 ± 0.012 when this ratio is corrected for decay). This ratio is in good agreement with that measured in Greenland ice, 0.017 ± 0.008. These ratios are also in agreement with the calculated values for the production of these isotopes by cosmic rays in the atmosphere: 0.013 ± 0.006. The contribution of cosmic dust bearing ^{26}Al seems small in comparison with the production of this nuclide in the atmosphere.*

Bombardment of atmospheric constituents by galactic cosmic rays produces two radionuclides that have million-year half-lives ($T_{1/2}$), ^{10}Be ($T_{1/2} = 1.5 \times 10^6$ years) and ^{26}Al ($T_{1/2} = 0.716 \times 10^6$ years) (*1*). The influx of cosmic dust can also bring to the earth some cosmogenic radionuclides such as ^{26}Al, ^{53}Mn ($T_{1/2} = 3.7 \times 10^6$ years), and ^{59}Ni ($T_{1/2} = 0.080 \times 10^6$ years), which are produced principally by the interaction of solar protons and α particles with cosmic dust (*2*). Pelagic sediments and polar ices are considered to be the best materials in which to detect these radionuclides (*1, 2*).

The measurement of such nuclides in marine sediments can furnish useful information about oceanic sedimentation rates and cosmic dust accretion rates in the last millions of years. It has been proposed that simultaneous measurements of ^{26}Al and ^{10}Be would be a good way to acquire such information (*3*).

Amin *et al.* (*4*) found the mean specific activities of ^{26}Al and ^{10}Be in two cores from the Pacific basin to be 0.5 and 4 disintegrations per minute (dpm) per kilogram of dry sediment, respectively, which correspond to an average $^{26}Al/^{10}Be$ ratio of 0.12 and imply that the ^{26}Al content is higher by an order of magnitude than that expected from the spallation of atmospheric argon. Indeed, Lal and Peters (*5*) estimated the global production rates of ^{26}Al and ^{10}Be by spallation of atmospheric nuclei to be 8×10^{-9} and 8×10^{-7} dpm cm^{-2} year^{-1}, respectively, which corresponds to a $^{26}Al/^{10}Be$ ratio of 0.01. The high ^{26}Al content found by Amin *et al.* in the Pacific sediments was interpreted as a consequence of a considerable influx with cosmic dust (*6*). Wasson *et al.* (*7*) reported a ^{26}Al content of 0.8 dpm per kilogram of dry sediment. This high ^{26}Al content was also interpreted as a consequence of ^{26}Al influx with cosmic dust, although one cannot completely rule out the possibility that argon spallation is responsible for all the observed activity. McCorkell *et al.* (*8*), however, found that the $^{26}Al/^{10}Be$ ratio in Greenland ice was 0.017, which is an order of magnitude lower than the ratio obtained by Amin *et al.* (*4*). This low ratio can be explained as resulting entirely from spallation of atmospheric nuclei without the need to postulate a ^{26}Al influx with cosmic dust. Tanaka *et al.* (*9*) measured the mean specific activities of ^{26}Al and ^{10}Be in a core from the Pacific basin to be 0.02 ± 0.26 (*10*) and 4.4 ± 0.9 dpm per kilogram of dry sediment, respectively, which results in an average $^{26}Al/^{10}Be$ ratio of less than 0.06, the upper limit of the ^{26}Al activity being 0.28 dpm per kilogram.

In the past ^{26}Al in sediments was detected by measurement of coincidence events of two annihilation γ-rays (0.511 Mev), because the small NaI(Tl) crystals available then (about 7.5 by 7.5 cm) were extremely inefficient detectors of 1.8-Mev photons. This peak at 0.511-0.511 Mev is common for all positron (β^+) emitters such as ^{22}Na and ^{44}Ti and not necessarily specific for ^{26}Al. Perhaps remeasurements of the ^{26}Al contents of earlier samples in a more specific way with more sensitive instruments will contribute to the settlement of the question.

It was for this reason that we undertook remeasurements of the samples measured by Tanaka *et al.* (*9*). The samples are Al_2O_3 extracted from half (in vertical cutting) of a red clay core, 7.8 cm in diameter and 1 m long, which came from a depth of 5439 m at 23°07′N, 135°45′E. The Al_2O_3 content was vertically uniform throughout the core: 16.38 ± 0.32 percent (dry weight). The method of extraction and purification of aluminum has been described in (*9*). The chemical yield of aluminum was 72.2 ± 2.8 percent. The core was cut in four sections, each about 25 cm long. For the present mea-

Table 1. Measurements of ^{26}Al in an Al_2O_3 sample from Pacific sediment.

Energy (Mev)	Nuclide and efficiency	Count rate (10^{-4} count min^{-1})				Activity* (dpm per kilogram of dry sediment)
		Gross	Contribution		Net	
			Background	Thorium†		
		At Gif-sur-Yvette				
0.511-2.34	^{26}Al, 6%	423 ± 22	424 ± 18	0 ± 2	−1 ± 28	0.00 ± 0.14
		At Issy-les-Moulineaux				
0.511-2.34	^{26}Al, 5.6%	168.1 ± 6.8	152.6 ± 5.2	0 ± 1.6	15.5 ± 8.7	0.081 ± 0.046
0.511-1.81	^{26}Al, 1.9%	265.3 ± 8.6	257.6 ± 8.8	0 ± 0.7	7.7 ± 12.3	0.12 ± 0.19
0.511-0.511	^{26}Al (β^+), 6%	730 ± 14	729 ± 15	0 ± 2	1 ± 21	0.00 ± 0.10
0.583-2.61	$^{232}Th(^{208}Tl)$, 1.5%	769 ± 15	772 ± 12		−3 ± 19	

*The errors include all known sources of errors: counting statistics (1 standard deviation), counting efficiency (± 5 percent), and chemical yield (± 4 percent). †Contributions of thorium to the peaks at 0.51-2.34 Mev, 0.511-1.81 Mev, and 0.511-0.511 Mev are 8.5, 4.0, and 8.4 percent, respectively, of the count rate in the peak at 0.583-2.61 Mev.

Table 2. Summary of the results of ^{26}Al and ^{10}Be measurements.

Investigators	Activity*		$^{26}Al/^{10}Be$
	^{26}Al	^{10}Be	
	In Pacific sediment		
Present work† At Issy	0.081 ± 0.046	4.6 ± 0.9‡	0.018 ± 0.011
Present work† At Gif	0.00 ± 0.14	4.6 ± 0.9‡	< 0.03
Tanaka *et al.*§ *(9)*	0.02 ± 0.26‖	4.4 ± 0.9	< 0.06
Amin *et al. (4)*	0.46 ± 0.17	3.9 ± 0.2	0.12 ± 0.04
Wasson *et al. (7)*	0.81 ± 0.12		
	In Greenland ice		
McCorkell *et al. (8)*	0.32 ± 0.09	18.4 $^{+8.4}_{-4.8}$	0.017 $^{+0.007}_{-0.009}$

*The activities for Pacific sediments are expressed in dpm per kilogram of dry sediment; the activities for Greenland ice are expressed in 10^{-6} dpm per liter. †The present work was done on the first three of the four sections of Tanaka *et al.*, sections 1A, 1B, and 2A. ‡^{10}Be was measured by Tanaka *et al.* (9). §Means of the four sections 1A, 1B, 2A, and 2B. ‖See (*10*).

surements we combined the Al_2O_3 extracted from the first three sections, 1A, 1B, and 2A, which correspond to the depth from 0 to 73 cm. The weight of the sample was 55 g.

The isotope ^{26}Al decays by β^+ emission (85 percent) followed by emission of a 1.83-Mev γ-ray (99.7 percent) (*11*). The coincidence spectrum of ^{26}Al is characterized by three peaks: 0.511-0.511 Mev (which is common for all β^+ emitters), 0.511-1.83 Mev, and 0.511-2.34 Mev. The last peak is a sum-peak (2.34 Mev being the sum of 0.511 + 1.83 Mev) and the most specific of the three peaks for the detection of ^{26}Al. The isotope ^{208}Tl of the thorium family is the only nuclide which makes a significant contribution in this energy region by the Compton effect of its γ-rays at the peak 0.58-2.60 Mev.

The measurements were carried out with a low-level gamma-gamma coincidence spectrometer developed by Reyss *et al.* (*12*). The spectrometer consists of two semicylindrical NaI(Tl) scintillators (dimensions, 30 by 25 cm) with a 30 by 5 cm NaI (without Tl) light guide. Samples are placed between the two scintillators. These detectors are surrounded successively by a plastic scintillator 5 cm thick (in anticoincidence with the main detectors), 10 cm of B_2O_3-bearing paraffin, 2 cm of copper, 12 cm of iron, and 15 cm of lead. Coincidence spectra were obtained with a 4096-channel x-y biparametric pulse height analyzer. We used an automatic gain corrector which consists of a weak ^{137}Cs source and gain feedback system (^{137}Cs is a single γ-ray emitter which does not give coincidence counts.)

A preliminary measurement, which was carried out at Gif-sur-Yvette at a depth of 5 m.e.w. (meter water equivalent) showed a very low net count rate of ^{26}Al, less than 7 percent of the background, which corresponds to 0.00 ± 0.14 dpm per kilogram of dry sediment (Table 1). Therefore, further reduction of the background was necessary in order to obtain more precise results. Since most of this background was due to γ-rays caused by muon-induced neurons, we found that by placing the spectrometer in a limestone cavern at Issy-les-Moulineaux (3 km southwest of Paris) at a depth of about 80 m.w.e., it was possible to reduce the background count rates considerably (by a factor of 3).

For the background measurements, dummy samples of purified Al_2O_3 (or Lucite) of identical mass and similar shape were used (we found no difference between the background count rates of these two materials). Four series of counting measurements were made. In each series the count rates of the sample and the background Al_2O_3 (or Lucite) were measured alternately. The count rate of the sample was measured for 35,926 minutes and that of the background for 57,288 minutes.

Table 1 shows the final numerical results. Activity due to thorium was not detected in the present sediment sample. The ^{26}Al activity of the present sample was therefore determined from the result of the sum-peak: 0.081 ± 0.046 dpm per kilogram of dry sediment. The results obtained from the other two peaks showed larger statistical errors. Nevertheless, they are not inconsistent with the result of the sum-peak.

Our results are summarized in Table 2 along with earlier results. The earlier measurement of Tanaka *et al.* (*9*) which gave an upper limit, less than 0.26 dpm of ^{26}Al per kilogram of dry sediment, is not contradictory to our work. Nevertheless, we have greatly ameliorated the accuracy of measurement not only in the counting statistical errors but also in the quality of data by measuring more specific γ-rays of ^{26}Al. Combining the present ^{26}Al determination with the ^{10}Be determination made by Tanaka *et al.* on the same sample, we obtained a $^{26}Al/^{10}Be$ ratio of 0.018 ± 0.011. The age of the part of the core used in the present work (0 to 73 cm) is estimated to be between 0 and 3×10^5 years. Since the $^{26}Al/^{10}Be$ ratio decreases with a $T_{1/2}$ of 1.4×10^6 years, the corrected ratio for the decay is 0.019 ± 0.012. This ratio is in good agreement with the one obtained by McCorkell *et al.* (*8*) in Greenland ice, 0.017 (*13*) but conflicts with the result reported by Amin *et al.* (*4*), 0.12.

Earlier measurements, which indicated high ^{26}Al contents in marine sediments (*4*, *7*), were strongly criticized by McCorkell *et al.* We believe that the reported high values of Amin *et al.* and Wasson *et al.* for ^{26}Al in marine sediments are suspect.

The important point is that the $^{26}Al/^{10}Be$ ratios obtained from two entirely different sources (marine sediment and Greenland ice) are now in good agreement. Since the observed ratios are also in agreement with our predicted ratio of 0.013 ± 0.006 (*14*) for the production by cosmic rays in the atmosphere, the postulated high influx of ^{26}Al with cosmic dust (*2*) should be reconsidered. The contribution of cosmic dust–bearing ^{26}Al can be estimated to be 0.6×10^{-9} dpm cm^{-2} year^{-1} (*15*), which is small in comparison with the production of ^{26}Al in the atmosphere, 5×10^{-9} dpm cm^{-2} year^{-1}.

J. L. Reyss
Y. Yokoyama
Centre des Faibles Radioactivités, Laboratoire mixte Centre National de la Recherche Scientifique–Commissariat à l'Energie Atomique, 91190-Gif-sur-Yvette, France
S. Tanaka
Institute for Nuclear Study, University of Tokyo, Tokyo 188, Japan

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the tropical sea sediment (0 to 300,000 years old) and the result from the Greenland ice (100 to 300 years old) is what can reasonably be expected from the constancy of galactic cosmic rays in the last million years and from the fact that the $^{26}Al/^{10}Be$ ratios are compared: the ratio of the production rates $^{26}Al/^{10}Be$ in the atmosphere is practically independent of the geomagnetic latitude effect, and the two elements, aluminum and beryllium, show striking similarities in their chemical behaviors.

14. The earlier estimation of the ^{26}Al production in the atmosphere, 8×10^{-9} dpm cm^{-2} year^{-1} (*5*), was based on the cross section calculated from an earlier formula of G. Rudstam [*Philos. Mag.* **46**, 344 (1955)], which is good only to about a factor of 3. By using a more elaborate formula [R. Silberberg and C. H. Tsao, *Astrophys. J. (Suppl. Ser. 220)* **25**, 315 (1973)], which generally shows an agreement with experimental results to within +30 percent and −25 percent, we obtained a ^{26}Al production rate of 5.3×10^{-9} dpm cm^{-2} year^{-1}. The ^{10}Be production rate was estimated at $(4.2 \pm 1.4) \times 10^{-7}$ dpm cm^{-2} year^{-1} as an average of the estimation based on the use of radiochemically measured cross sections [B. S. Amin, S. Biswas, D. Lal, B. L. K. Somayajulu, *Nucl. Phys. A* **195**, 311 (1972)] and that based on the use of isotopically determined cross sections [G. M. Raisbeck and F. Yiou, *Phys. Rev. C* **9**, 1385 (1974)], 4.7×10^{-7} [B. S. Amin, D. Lal, B. L. K. Somayajulu, *Geochim. Cosmochim. Acta* **39**, 1187 (1975)] and 3.6×10^{-7} dpm cm^{-2} year^{-1}, respectively. From these results a $^{26}Al/^{10}Be$ ratio of 0.013 ± 0.006 was obtained for the production in the atmosphere.

15. Based on the cumulative meteroid flux determined by B. G. Cour-Palais [*NSAS Spec. Publ. 330* (1973), p. 22-1] from the Apollo window meteoroid experiment, we estimated a cosmic dust accretion rate of 35 ton/day and a saturation factor of about 50 percent. [For this estimate, we used the flux-mass curves in figure 21-4 of Cour-Palais: the solid line (NASA model curve) for particles of $> 10^{-8}$ g and the dashed line for smaller particles.] This meteoroid flux, in agreement with lunar sample microcrater data (F. Horz, D. A. Morrison, D. E. Gault, V. R. Oberbeck, W. L. Quaide, J. F. Vedder, paper presented at the Soviet-American Conference on the Cosmochemistry of the Moon and Planets, Moscow, 4–8 June 1974) may be uncertain by as much as a factor of 3. Assuming a solar proton flux of J (energy > 10 Mev) = 100 proton cm^{-2} sec^{-1} per 4π with a shape factor of R_0 = 100 Mv or J = 70 with R_0 = 150 Mv [Y. Yokoyama, J. Sato, J.-L. Reyss, F. Guichard, in *Proceedings of the Fourth Lunar Science Conference*, W. A. Gose, Ed. (Pergamon, New York, 1973), vol. 2, p. 2209], we obtained a saturated activity for ^{26}Al of 0.5 dpm per gram of cosmic dust. Combining these data, we estimated an influx of 0.6×10^{-9} dpm cm^{-2} year^{-1}, which is about 10 percent of the ^{26}Al production in the atmosphere.

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Density Maxima in High-Pressure Supercooled Water and Liquid Silicon Dioxide

Abstract. *With glass capillary pressure vessels it has been possible to study the effect of pressure on the temperature of maximum density (TMD) and on the "sharpness" of the density maximum in liquid H_2O and D_2O in the important but little-studied supercooled regime. A pressure of 1200 bars produces a 33°C depression of the TMD in these liquids and a considerable reduction in sharpness. Comparison with the rather flat density maximum for liquid SiO_2 supports the notion that the presence or absence of density anomalies in "tetrahedral" liquids depends on the average bridge-bond angle, which is evidently unusually large in water at normal pressure.*

The liquid states of H_2O and SiO_2 are unusual, although by no means unique, in their density-temperature relations insofar as both liquids exhibit density maxima (*1, 2*). In H_2O at a pressure of 1 atm the density maximum occurs in the stable liquid region, whereas in SiO_2 the maximum is observed only in the supercooled state. It has been common to assume in each case that the anomaly arises from the tendency of these liquids to establish an expanded tetrahedral network structure as the temperature decreases. The details of this structuring are clearly vital to an understanding of the properties of these important liquids.

In a recent report (*3*) we speculated, on the basis of the pressure dependence of the homogeneous nucleation temperature of water, that the difference in the temperature of maximum density (TMD) relative to the melting point, as well as a difference in the "sharpness" of the volume variations about the maximum in each case, was due to differences in the average "bridge-bond" angle, O···H–O or Si–O–Si. We present here some observations for D_2O on the pressure dependence of the TMD and of the density about the TMD, which tend to support the above suggestion. We report on D_2O rather than on H_2O because of the greater pressure range over which the TMD can be followed before the supercooling limit for our method is exceeded.

The new measurements cover the temperature (T) range from 30°C to −30°C and the pressure (P) range from 1 to 1200 bar. Because of the need to make the most important measurements at high pressures under conditions where the liquids were metastable, we found it necessary to develop an unusual though very simple high-pressure technique, which we describe briefly.

To avoid premature crystallization, small samples must be used (*4*). For the measurements described here we satisfied this condition by confining the samples in fine glass capillaries with a bore of ~ 90 μm. When freshly pulled from tubing 9 mm in outside diameter and 2 mm in inside diameter, these capillaries prove to be capable of withstanding internal pressures well in excess of 2 kbar without rupture. Thus the glass capillary can serve as the sample container, the crystallization inhibitor, and the pressure vessel at the same time. Because the pressure vessel is transparent, volume (V) measurements may be made by direct visual observation of the position of the mercury meniscus. With this capillary pressure vessel it is possible to extend a "see-through" volumetric technique for the study of supercooled water developed by Speedy and Angell (*5*) to the 2-kbar pressure range. Capillary tubes were selected for uniformity of diameter and calibrated. Triply distilled water was introduced and isolated by means of a mercury slug, and the filled capillary was sealed with epoxy resin into a steel connecting link to a hydraulic high-pressure system. We then monitored the position of the mercury meniscus relative to a series of fiducial marks on the capillary at various pressures and temperatures, using a cathetometer external to a thermostating bath.

Using capillaries of length 0.2 to 1.0 m, we could determine compressibilities (*6*)

$$-\frac{1}{V}\,(\partial V/\partial P)_T$$

to ± 1 percent. It was not possible to determine expansivities

$$\frac{1}{V}\,(\partial V/\partial T)_P$$

with as high a degree of accuracy, because the volume is very sensitive to pressure and the pressure on the Heise Bourdon gauge could not be read more accurately than ± 2 bars. However, the volume could be determined to ± 0.01 percent, sufficient to characterize the behavior of D_2O in the vicinity of the density maximum. Both compressibilities and expansivities could be studied down to temperatures in the range −20° to −30°C depending on pressure, before the measurements had to be terminated because of sample crystallization. This event tended to be destructive of calibrated capillaries and was therefore to be avoided as far as possible.

We determined the TMD for each pressure by computer-fitting the column length versus temperature data to a fourth-degree polynomial and finding the extremum. Corrections for the thermal expansivity of the glass are negligible, but it was necessary to correct for the dimensional changes of the capillary with pressure. We did this by calibrating each run, using the PVT data of Fine and Millero for water at ordinary temperatures (*7*).