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Factors influencing ^{7}Be accumulation on rock varnish

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Abstract. Rocks coated with desert varnish were translocated from Scottsdale, Arizona, and Panamint Valley, California, to a fenced-in plot near Biosphere 2 where they were allowed to accumulate a new crop of the 53 day half life, cosmic ray-produced ^{7}Be. Those exposed to precipitation accumulated several times more of this isotope than those shielded from precipitation. No significant difference in ^{7}Be accumulation was observed between a set which was UV irradiated (in an attempt to kill resident bacteria) and a set which received no UV irradiation. This experiment suggests that 62 ± 10 percent of the beryllium accumulated on the varnish was supplied by precipitation and 38 ± 10 percent by some combination of dew, dust, and aerosols. If bacteria are, as has been proposed, responsible for varnish growth, then either our UV irradiation was inadequate to squelch their activity or the ^{7}Be we measured had not yet been built into the varnish.

Introduction

Because of its extremely slow rate of accumulation (a few micrometers per millennium) [Liu and Broecker, 2000], it has been difficult to characterize either the source of the ingredients or the depositional mechanism for rock varnish growth. As varnish forms only on those portions of rocks exposed to the atmosphere and since the composition of the varnish does not correlate with that of the rock substrate [Potter and Rossman, 1977, 1979; Allen, 1978; Perry and Adams, 1978; Dorn and Oberlander, 1982; Moore and Elvidge, 1982; Krinsley et al., 1995; Krinsley, 1998], it is clear to us that the constituents are delivered in rain, snow, dew, dust, and aerosols. The ten-fold enhancement of the concentrations of large lithophile elements over those of Mg, Al and Si (relative to those in average igneous rock or shale) suggests that significant chemical separations occur during the conversion of the input material into varnish [Fleisher et al., 1999]. Further, in order to explain the difference in chemical composition of varnish formed in glacial times (higher in Mn and Ca and lower in Mg, Si and Al) and that formed in interglacial times (the opposite) [Liu and Dorn, 1996; Fleisher et al., 1999; Liu et al., 2000], either the composition of the material delivered from the atmosphere or the nature of this chemical transformation must be dependent on climate.

In a previous paper [Fleisher et al., 1999], we showed that varnish is accumulating short-lived radioisotopes (i.e., ^{210}Pb and ^{137}Cs) and anthropogenic metals (i.e., Pb and Zn). We also have shown that varnish accumulates a few percent of the cosmogenic ^{10}Be carried from the atmosphere to the Earth's surface (see Table 1). On the basis of this latter measurement and the approximate 1:1 ^{7}Be/^{10}Be ratio in rain [Brown et al., 1989] we predicted that ^{7}Be (53 day half life) could be employed to elucidate the factors influencing varnish growth. The required surface area would be about 100 cm^{2}.

Establishment of a Rock Varnish 'Garden' at Biosphere 2

Based on logistic concerns, we decided against conducting interactive studies at locales where varnish forms. Rather, we transported varnish-coated rocks from two locales (McDowell Mountain near Scottsdale, Arizona and Panamint Valley, California) to a desert site on the Biosphere 2 property. Eight such rocks were deployed in a fenced-in area created for this purpose (see Figure 1A). They were placed in the same orientation and depth in the soil as in their original habitat. Four were equipped with shields which were triggered by precipitation to move into place. In the absence of rain (or snow), these shields retracted (see Figure 1B). In order to test if bacteria are responsible for varnish growth [Krumbein and Jens, 1981; Taylor-George et al., 1983; Dorn, 1984; Palmer et al., 1986; Hungate et al., 1987; Nagy et al., 1991; Grote and Krumbein, 1992; Krinsley et al., 1995], four of the varnished rocks were irradiated with UV light for 5-minute periods once each week. The unit used was an 8 watt 254 nM germicidal lamp that yields 1930 micro watts/cm^{2} at 15 cm range. We held the lamp approximately 7 cm above the varnish surface.

The varnished rocks were emplaced at Biosphere 2 on April 10, 2000. Two were harvested on October 2, 2000, and the other six on January 9, 2001. They were promptly shipped to the University of South Carolina for measurement.

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Table 1. ^{10}Be measurements made on varnish scraped from rock surfaces by accelerator mass spectrometry. The global production rate of ^{10}Be is estimated to be $1.2 \infty 10^{6}$ atoms per square centimeter per year [Brown et al., 1992]. However, because of the lower than average precipitation rate characterizing these desert sites, the actual delivery rate is likely somewhat lower than this global average. Hence, the capture efficiencies given in the last column of this table are likely minima.

Sample Location	Latitude/ Longitude	Altitude (m)	Surface Area (cm^2)	Varnish Weight (mg)	Be Carrier (mg)	^{10}Be/Be (at./at.)	^{10}Be Content (at./cm^2)	Basal Age[§] (ky)	^{10}Be Accum. Rate (at./cm^2yr.)	Accum. Rate/ Prod. Rate
Darwin Pass, California	36°21'20" N/ 117°37'54" W	1500	3.41	6.1	1	2.35∞10-11	0.46∞10^{9}	~11	4.2∞104	0.035
Grassy Mountain Utah	40°44'50" N/ 113°08'50" W	1350	1.92	5.38	1	1.04∞10-11	0.36∞10^{9}	~11	3.3∞104	0.028
Fish Lake Valley Nevada	37°55'54" N/ 118°08'45" W	1650	2.21	4.65	1	0.97∞10-11	0.29∞10^{9}	~11	2.6∞104	0.022
Papago Park, Arizona	33°35'30" N/ 111°55'30" W	350	3.23	3.81	1	0.71∞10-11	0.15∞10^{9}	~11	1.4∞104	0.012

[§]The base ages of these varnishes were estimated from their microstratigraphies that are Holocene in age (cf. Liu et al., 2000).

Leaching Experiments

To remove ^{7}Be and ^{210}Pb from the surface of rocks coated with desert varnish we leached the surface with HCl. The rock was supported in a plastic beaker and the entire surface (150-300 cm^2) was wetted with 20 ml concentrated HCl dispensed from a dropper. The excess acid was collected in the beaker. Next the surface was wetted again with 6M HCl and the acid collected in the beaker. Finally the wetted surface was washed with 150-200 ml DI water. This leaching procedure was repeated for one sample to determine if all of the ^{7}Be was removed by the first leach. It was.

The acid and wash were evaporated to near dryness and taken up in DI water. NH_4OH was added to raise the pH to 8 and precipitate Fe and Mn hydroxides which carried Be and Pb. The precipitate was transferred to a counting vial, centrifuged and sealed.

The counting vial was placed in the well of an intrinsic germanium detector and counted for 1-3 days. The gamma spectra was analyzed using the program HYPERMET [Phillips and Marlow, 1976]. Standards run in the same geometry were used to calibrate the detector.

Results

As listed in Table 2, the results send a clear message. The four varnished rocks with rain shields accumulated only 38 ± 10 percent the amount of ^{7}Be accumulated on those without shields. This conclusion holds whether the ^{7}Be activity is normalized to the area leached or to the 22 year half life ^{210} Pb activity of the leach (the ^{210}Pb accumulated at the original sites must dominate that accumulated during the relatively short exposure at Biosphere 2). The four UV irradiated varnishes accumulated roughly the same amount of ^{7}Be as those which received no UV irradiation.

It is interesting to note that the ratio of ^{7}Be to ^{210}Pb ratio was twice as high in the Panamint varnishes as it was in the Scottsdale varnishes. A likely explanation is related to the fact that precipitation at Scottsdale is higher than that at Panamint. The ^{210}Pb activities (per unit area) of the two sets of varnished rocks reflect this difference. Thus, when placed in the higher precipitation environments at Biosphere 2, the radionuclides accumulated at a higher rate than they did at Panamint (but at a comparable rate to that at McDowell Mountain).

Discussion

One puzzling aspect of these results is that there was far less rainfall between April 10 and October 2 (the time the first two samples were harvested) than between October 2 and January 9

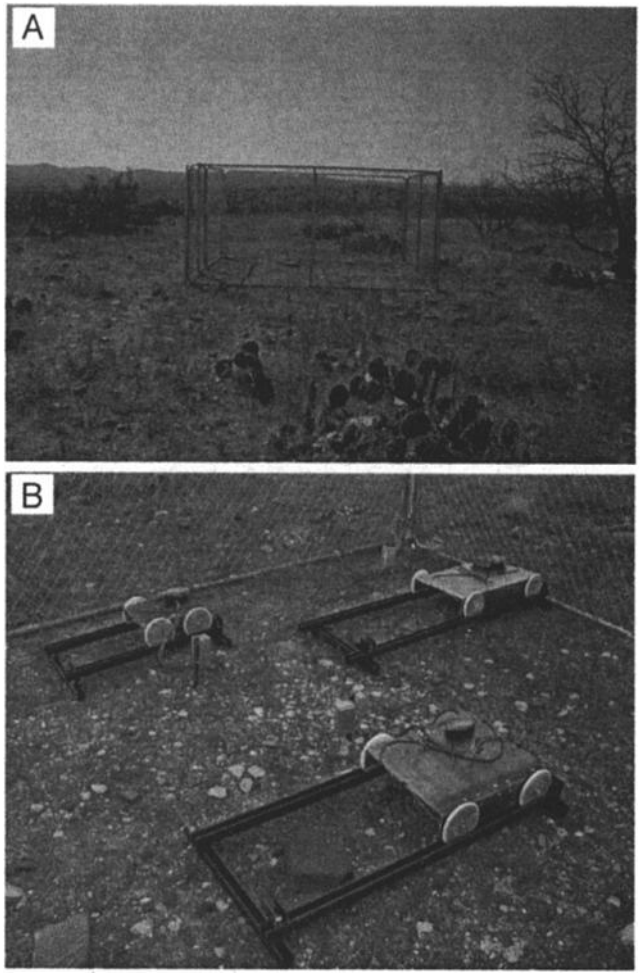

Figure 1. A. Photo showing a fenced-in varnish garden at Biosphere 2 in the Sonoran Desert of southern Arizona. B. Photo showing placement of the translocated rocks and of the moveable shields.

Table 2. Summary of the ^{7}Be and ^{210}Pb measurements made on samples exposed in the Biosphere 2 varnish garden. The ^{7}Be counting efficiency is 1.15%. This is the product of the detector efficiency (11.1%) and gamma intensity (10.39%). For ^{210}Pb the counting efficiency is 3.04%. This is the product of the detector efficiency (including self absorption) (75.1%) and gamma intensity (4.05%). Each sample was counted for 1-3 days.

Sample Number	Rain	UV	Date Removed	Date Counted	Area Leached (cm^2)	^{210}Pb (dpm/cm^2)	^{7}Be (dpm/cm^2)	^{7}Be/^{210}Pb	Fraction Attributable to Rain
Panamint Valley, California (35°59'38"N, 117°12'58"W, 350 m)									
PL-1	Yes	No	2-Oct-00	9-Oct-00	221	1.44	0.52	0.361	0.72
PL-3	No	No	2-Oct-00	6-Oct-00	154	2.23	0.227	0.102	-
PL-4	Yes	Yes	9-Jan-01	20-Jan-01	127	1.65	0.396	0.24	0.51
PL-5	No	Yes	9-Jan-01	30-Jan-01	202	1.79	0.212	0.118	-
Scottsdale, Arizona (33°35'46"N, 111°49'03"W, 500 m)									
MTN-3	Yes	No	9-Jan-01	24-Jan-01	280	3.1	0.393	0.126	0.69
MTN-4	No	No	9-Jan-01	29-Jan-01	312	3.94	0.155	0.039	-
MTN-5	Yes	Yes	9-Jan-01	23-Jan-01	286	4.17	0.497	0.119	0.61
MTN-2	No	Yes	9-Jan-01	18-Jan-01	185	3.98	0.185	0.046	-

(the time the remaining 6 samples were harvested) (see Table 3). As shown in Table 2 where the rain results are corrected for ^{7}Be radiodecay (from day of rain to the day of counting), the varnishes harvested in early January received 58.2/15.1 or 3.9 times more decay corrected rain than those harvested in early October. Yet in the case of the Panamint varnish, the samples harvested in October had nearly half again as much ^{7}Be as those harvested in January. One possible explanation could be that the January set was UV irradiated while the October set was not. However, as the UV irradiated varnish set from Panamint has only slightly higher ^{7}Be activities than the unirradiated set, this is not likely the explanation. Another possibility is that the ^{7}Be carried by the heavy October rains largely ran off. It is even possible that these heavy rains removed previously accumulated ^{7}Be.

Table 3. Summary of the precipitation as measured at the site of the varnish garden. These amounts are corrected in order to account for the decay of ^{7}Be between the rain event and counting.

Date	ΔT (Days)	Rain (mm)	Decay Cor. To Oct. 7	Decay Cor. To Jan. 24
10-Apr-00	0	Deploy.		
Aug. 28 00	140	12.2	7.5	2
Aug. 29 00	141	8.4	5.2	1.4
Sept. 28 00	171	1.4	1.3	0.3
Oct. 1 00	174	1.2	1.1	1
Oct. 2 00	175	Harvest	Total 15.1	
Oct. 7 00	180	Count		
Oct. 8 00	181	3.7		1
Oct. 9 00	182	10.8		3.1
Oct. 10 00	183	6.1		1.7
Oct. 11 00	184	36.9		10.7
Oct. 19 00	192	7.5		2.4
Oct. 21 00	194	24		7.9
Oct. 27 00	200	19.2		6.8
Oct. 30 00	203	10.2		3.7
Nov. 4 00	208	40		15.7
Jan. 6 01	271	0.6		0.5
Jan. 9 01	274		Harvest	Total 58.2
Jan. 24 01	292		Count	

Another puzzle is that the accumulation rate of ^{7}Be is a factor of 10 higher than would be predicted from the ^{10}Be uptake rates shown in Table 1. As ^{10}Be has a half life of 1.6×10^{6} years its extent of incorporation is not altered by loss to radiodecay. Hence while the ^{7}Be we measured may have been merely absorbed onto the varnish surface the ^{10}Be we measured was incorporated in the varnish. The average ^{7}Be activity in Table 2 converts to 5×10^{4} atoms/cm^2. As this represents the accumulation over only 53/.693 or 76 days it corresponds to 25×10^{4} atoms/cm^{2}yr. The average for ^{10}Be was only 2.5×10^{4} atoms/cm^{2}yr. Yet the production ratio of these two cosmogenic isotopes is close to unity. One possible explanation for this difference is that the ^{7}Be atoms we measured have yet to be incorporated into the varnish. Rather they are absorbed on the surface. Were they not lost to radiodecay only 10 percent of those ^{7}Be atoms absorbed would be built into the varnish.

Our plan is to continue the field exposure program attempting to determine the source of the non-rain component and to initiate a laboratory study where delivery to the varnish surface is by artificial rain tagged with radioisotopes of a number of elements (including ^{7}Be). The objectives will be to determine differences in chemical affinities and the degree to which isotopes absorbed can be removed by tracer-free rain.

Although inconclusive our results suggest that the ingredients for varnish are likely delivered not only in rain but also in some combination of dew, dust, and aerosols. Our ^{7}Be analog appears to have a major drawback in that our results bear on only the first step in the incorporation process (namely absorption onto the varnish surface). The combination of ^{7}Be and ^{10}Be results suggests that only about 10 percent of the absorbed beryllium gets incorporated into the varnish.

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