

Broecker Brief

Source of the Manganese in Rock Varnish

Rocks in desert regions are often coated with what is called rock varnish. This slow-growing coating consists of a mixture of fine clay minerals and a manganese-rich cocktail of large lithophile elements. As shown by the large variations in the Mn content, the ratio of these two contributors has varied with time. The contribution of the Mn-cocktail end member relative to that of the clay-mineral end member appears to increase with rainfall.

Rock varnish shares features associated with sea floor Mn nodules. Both grow at the rate of a few microns per thousand years (i.e., a few molecular layers per day). Both incorporate Th and U in roughly the proportions found in igneous rocks (i.e., 4 to 1). Both are enriched in large lithophile elements. One prominent difference is that the element barium is highly enriched in rock varnish but not in manganese nodules. Another is that nodules many million years old are common on the sea floor but rock varnish older than 50 kyrs is rare.

Much of what we know about rock varnish is based on studies by Tanzhuo Liu. His PhD thesis at Arizona State University involved developing a procedure to make ultra-thin sections of varnish. Using these sections he is able to study its chemical layering. His original work was largely from various sites in the Great Basin. Upon receiving his PhD degree in 1994, T.L., as we call him, came to Lamont-Doherty as a postdoctoral fellow. Except for one three-year period, he has remained there ever since. He has been able to extend the geographic coverage of his rock varnish collection to China, Israel, Mongolia, Ethiopia and Argentina. And working with me and a number of my geochemically-oriented friends, he has been able to gather important clues regarding the origin of rock varnish.

As there is no way to directly date the varnish itself, T.L. has greatly benefited from the advent of precise ^{10}Be dating of boulders on moraines. They provide precise initiation times for varnish growth. Prior to this, he had to rely on radiocarbon dates on material associated with the rocks on which varnish formed.

Our assumption that rock varnish is a two-component mixture is based on two sets of observations. One is that crystalline clay minerals have been identified in varnish. Further, T.L. has shown that the ^{40}Ar to ^{40}K ratio in bulk varnish requires that these minerals are tens of millions of years old (just as they are in loess and in marine clays). So we assume that the K, Na, Mg, Ca, Al and Si are housed in clay minerals. The excess Mn, Be, U, Th and other large lithophile elements are part of the aerosol cocktail.

The other is that varnish contains short lived isotopes (^7Be , ^{210}Pb , ^{137}Cs). It also contains anthropogenic plutonium and lead. We assume these anthropogenics are carried by the same aerosols which deliver the Mn cocktail. We further assume that these aerosols carry the large lithophile elements (including Th and U in their igneous rock ratio). I emphasize the lack of a large separation between these two elements because, while uranium is moderately soluble, thorium is notoriously insoluble.

One other thing that merits mentioning is that an experiment conducted in the desert near Biosphere 2 showed that about half of the ^7Be (a 57-day half-life cosmogenic isotope) contained in varnish is delivered by the infrequent rains and the other half by dry deposition in between these rains (perhaps by aerosols trapped in morning dew).

I write this 'brief' in hope of luring someone to take on this subject in a serious way for there are many unanswered questions.

- 1) What is the mechanism for the large enrichment of Mn and Ba in aerosols?
- 2) Why aren't Th and U separated?
- 3) Do these aerosols carry the common thorium which plagues the ^{230}Th dating of subaerial exposed tufas (but not the ^{230}Th dating of white CaCO_3 s which are protected from surface exposure?)
- 4) Can the plutonium, excess lead and other anthropogenic substances currently accumulating in varnish serve as an environmental archive?
- 5) Is there anything of interest to be learned from isotopic measurements on oxygen, uranium, magnesium, calcium...?

- 6) If, as T.L. suspects, the variations in the composition of varnish are related to variations in rainfall, and if, as he contends, these variations are correlated over wide areas, then can they be used to date archeological objects and can they constrain the climate conditions under which they formed?

T.L. has a large archive of varnish samples and is eager to share them.



Figure 1. Tanzhuo Liu known as T.L.



Figure 2. The upper pale yellow varnish formed during the Holocene. The lower orange and black varnish formed during the LGM and deglacial periods.

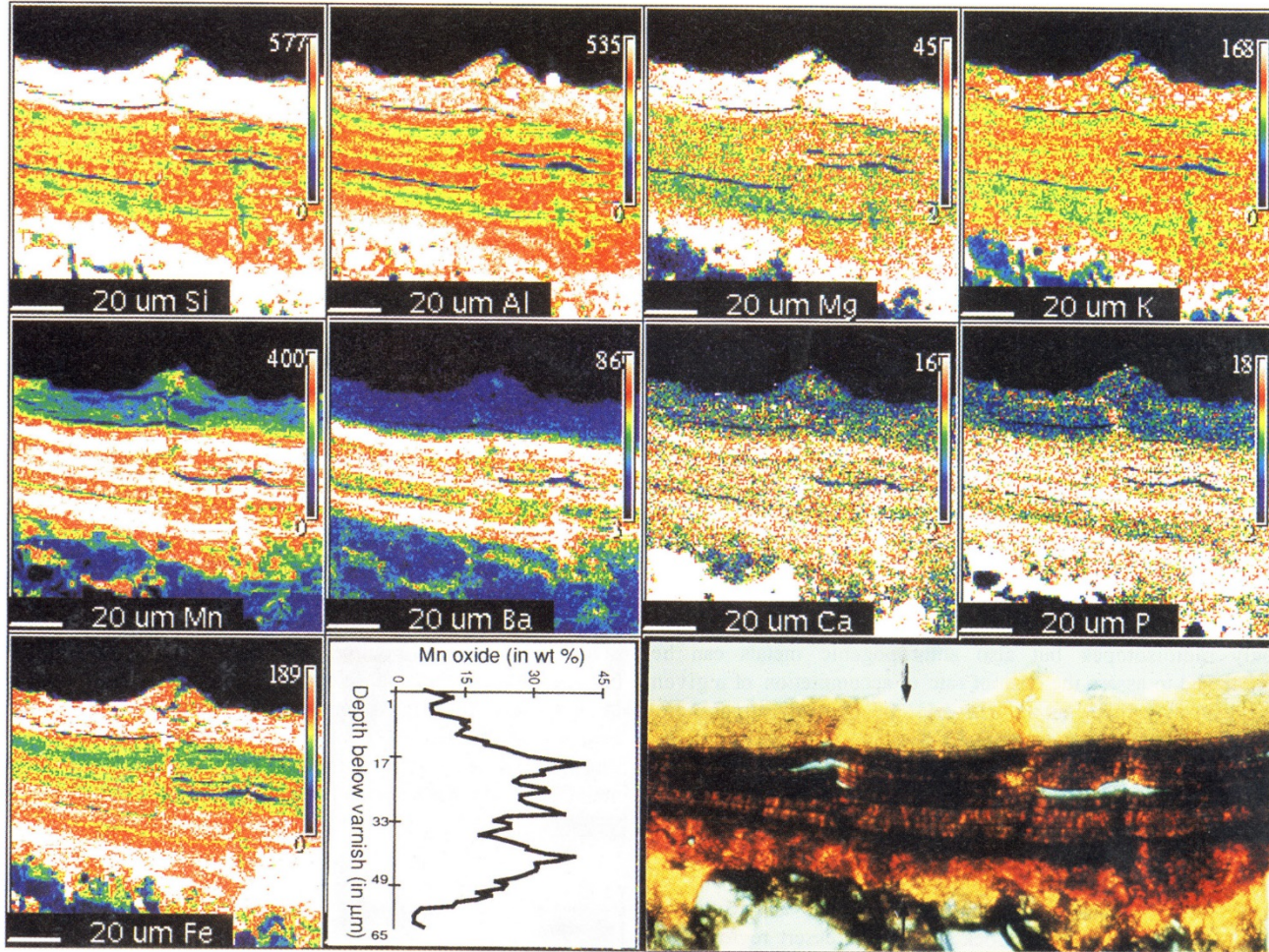


Figure 3. Element concentration maps for the varnish shown at the lower left.

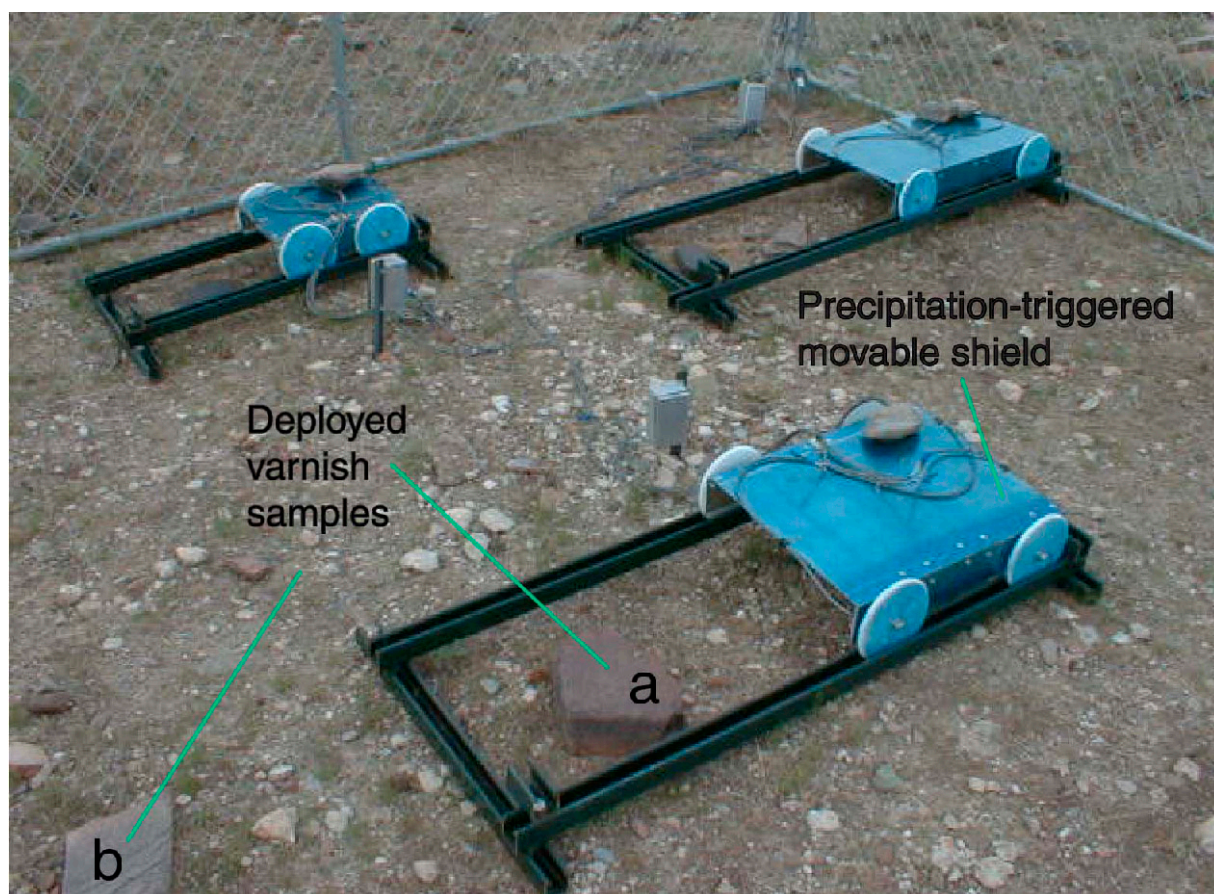


Figure 4. Set up for the ^7Be experiment.

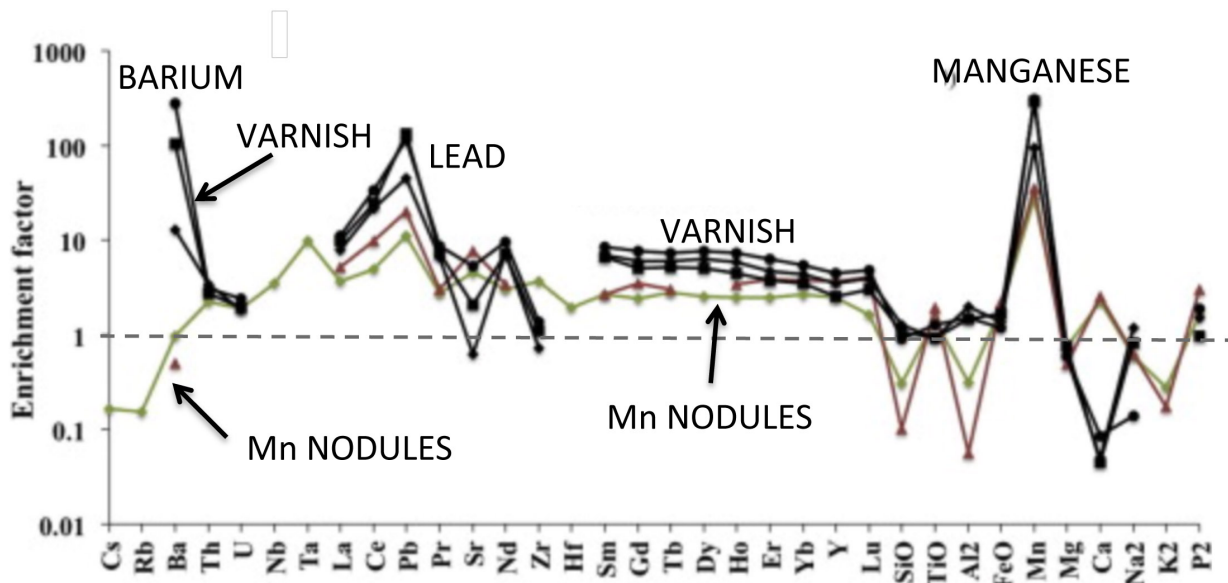


Figure 5. Enrichment factors with respect to magnesium in average Earth crust for a series of elements in rock varnish and in manganese nodules. Note that lead is highly enriched in both, barium is enriched in varnish but not in nodules, uranium and thorium are moderately enriched, and silica is highly depleted in nodules. The absence of a separation of highly insoluble thorium from moderately soluble uranium is puzzling.


	EARTH ROCKS	ROCK VARNISH	ENRICHMENT
U ppm	3	20	~7
Th ppm	12	70	~ 6
Th / U	4.0	3.5	—
		 AVERAGE	

Figure 6. Enrichment factors for U and Th in rock varnish. Note that little separation between these elements occurs during the formation of the Mn cocktail.