



Biogenicity inferred from microbialite geochemistry

Microbes^{1,2} utilise and/or concentrate diverse metal cations, whose detection may become a potent tool for reconstructing microbial processes and, in particular, for establishing the genesis of ancient carbonate rocks that were produced by microbes. Such rocks, termed microbialites, consist of trapped and bound sediment and, importantly, carbonate minerals precipitated as accidental byproducts of metabolic or decay processes within biofilms³. Where trace metals are predictably incorporated

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into microbialites, they may reflect biofilm processes and allow interpretation of preserved carbonates. Holocene (about 5-6,000 years old) microbialites that formed in reef cavities in the Great Barrier Reef (GBR)⁴ faithfully incorporated high concentrations of rare earth elements and yttrium proportional to their abundance in shallow seawater⁵. Ancient microbialites display similar behaviour^{6,7}.

In this paper we demonstrate that the inner transition elements V and Cr were incorporated into the Holocene GBR microbialites in abundances that discriminate the microbial carbonate from co-occurring skeletal carbonates and from theoretical abiotic carbonates. Our initial findings hold great promise for understanding the origins of ancient microbialites (i.e. biogenic versus abiogenic), which in many cases are controversial^{8,9}. New geochemical tools for recognising and interpreting ancient microbialites are critical for understanding earth history and especially for establishing the origin of proposed extraterrestrial microbialites¹⁰.

Reefal carbonates (52 microbialite, 3 scleractinian coral, 2 coralline red alga, 2 *Tridachna* clam) were analysed for trace element concentration using inductively coupled plasma mass spectrometry⁵. Microbialite samples have variable, but consistently elevated, V and Cr contents relative to measured skeletal carbonates that formed in the same ambient seawater. Concentrations of V and Cr were compared to that of Ba (Figure 1) because Ba is readily substituted for Ca²⁺ in the carbonate lattice and concentrations of Ba and Sr are highly correlated across all samples ($r^2 = 0.926$) suggesting that different sample types did not significantly

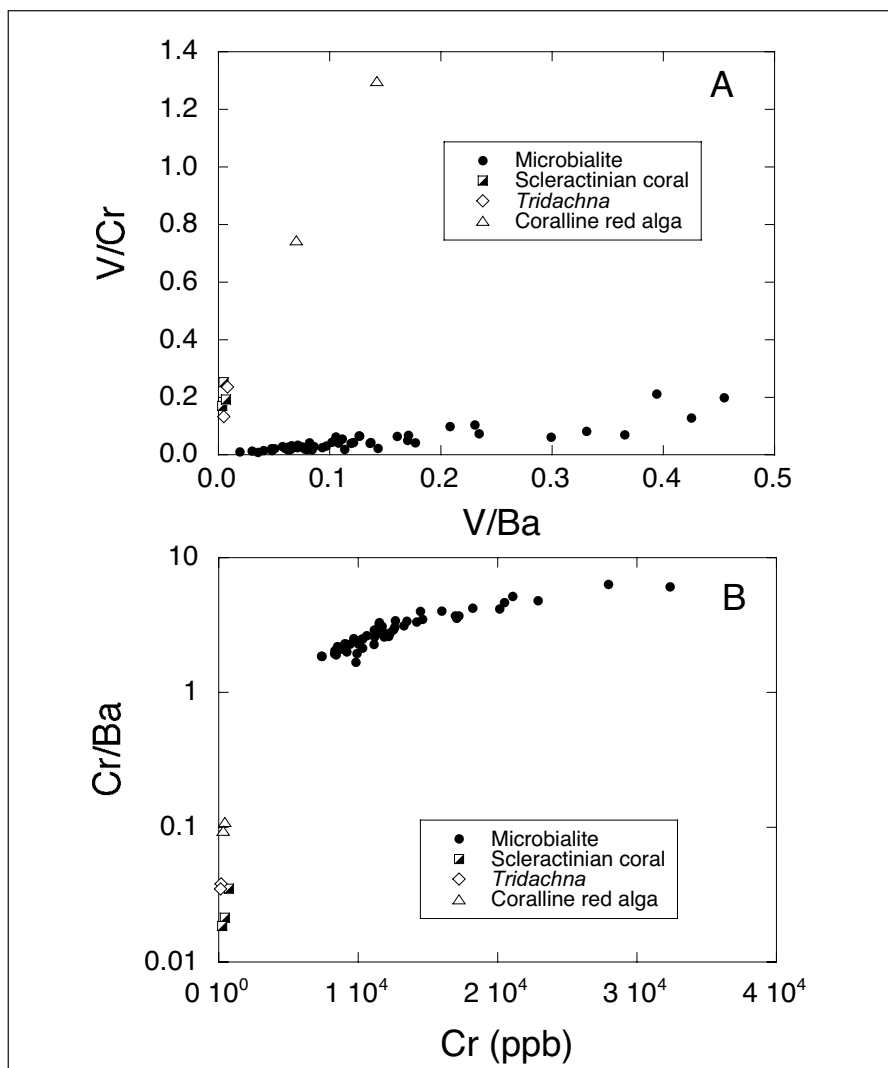


Figure 1. Trace element cross plots for reefal carbonates. Note that microbialite trace element behaviour differs from that of skeletal carbonates in both A and B.



discriminate against either element. Hence, Ba serves as a normalisation standard across the sample types.

Microbialite Cr concentrations are uniformly higher than those of other sample types. Microbialite Cr/Ba ratios (1.7-6.4) are vastly higher than those of skeletal carbonates (0.02-0.11). Carbonate V concentrations are typically close to analytical detection limits, but, on average, microbialite V/Ba is higher (0.131) than in skeletal carbonate (scleractinian coral=0.005; *Tridachna*=0.007; red algae=0.106).

A number of microbes and larger eukaryotes use and/or accumulate V^{1,2}. Significantly for the Holocene microbialites, V is concentrated by ascidians in tunichrome blood pigment¹¹. The occurrence of ascidian spicules in sampled microbialites complicates their interpretation. The V/Ba ratio of the carbonates plotted vs. the V/Cr ratio (Fig. 1a) defines a strong linear correlation for microbialites ($r^2=0.770$) and for skeletal samples ($r^2=0.992$), indicating mixing of a V-rich component (probably related to co-occurring ascidians) with an ambient component much poorer in V. Significant V in the red algae may relate to haloperoxidase¹.

The most significant feature in Figure 1a is that the microbialite trend is very distinct (at much lower V/Cr) from that of skeletal carbonates, reflecting much stronger microbialite Cr enrichment. Cr enrichment is also expressed on the Cr/Ba vs. Cr plot (Figure 1b). Microbialite Cr enrichment is apparently related to enrichment in other cations, such as Y ($r^2=0.519$). Many bacteria reduce the highly toxic Cr(VI) to the less toxic, less soluble Cr(III), in some cases for respiration, but few bacteria accumulate Cr².

The high concentrations of Cr in GBR microbialites suggest active

accumulation. Sulphate reducing bacteria may be responsible. Dissimilatory sulphate reduction can induce carbonate precipitation³. Some sulphate reducing bacteria utilise Cr(VI) as an electron receptor¹², but H₂S production may reduce chromate incidentally². The low solubility of resulting Cr(III) may have led to its incorporation in the microbialites.

Our data show that trace element chemistry not only discriminates between microbial and hydrothermal origins for carbonates, but that microbialites may contain trace metal signatures that reflect the biochemistry of particular biofilms. Data for additional transition metals will undoubtedly shed further light on issues such as biogenicity.

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