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Provenance and Colour of La Tène and Hallstatt period fibulae beads

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Background:

Fibulae beads from Hallstatt and La Tène ages were studied referring to material questions and provenance. Besides red and black beads, which could be evidenced as mostly not of organic origin, organic beads show white colour, which is uncommon for precious corals.

Archaeological theories supposed that white fibulae beads exist because of post-mortem bleaching processes or treatments of originally red corals.

We analyzed original red corals and submitted them to experimental procedures gaining information of possible bleaching methods, such as heating, chemical treatment with Na_2SO_4, $(NH_4)_2SO_4$, NaOH, $KMnO_4$, and H_2S_x related reactions simulating cyanobacteria.

Analytics:

Original red corals as well as white fibulae beads from Langenau in South Germany (Landesmuseum Württemberg, Stuttgart) and Dürrnberg in Austria (Keltenmuseum Hallein) show Mg-containing Calcite and organic Polyenes.

Using Raman Spectroscopy, different C-chain lengths and chain length combinations of Polyenes can be distinguished.

Red corals and white coral beads contain Polyenes with a C-chain length between $8 < N_{eff.} < 12$ (after Barnard *et al.* 2006). The precious corals Corallium rubrum and elatum show a chain length $N_{eff.} = 10$, the organ pipe coral shows a mixture of $N_{eff.}$ between 11 and 12.

Exceptions are fibulae beads from locations in Central Germany like Hänichen (Naturkundemuseum Leipzig), Kleinkorbetha (Landesamt für Denkmalpflege und Archäologie Sachsen-Anhalt, Halle) and Gräfenhainichen (Kreismuseum Bitterfeld): they consist of pure Mg-free Calcite without Polyenes. Therefore, these beads are probably attributed to fossil material, limestones or primary aragonitic corals transformed to Calcite by meteoric water.

Mg-containing Calcite and Polyenes

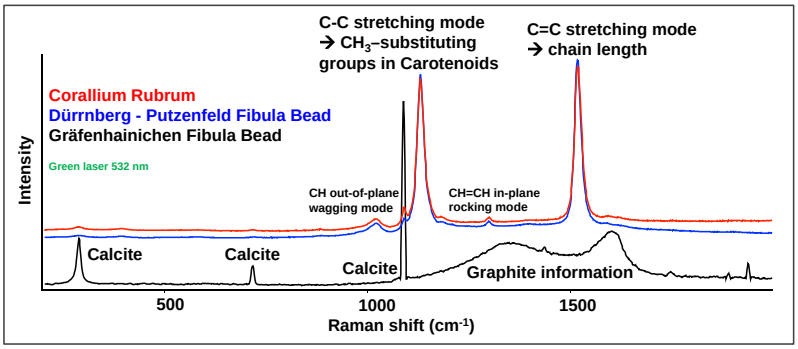
Dürrnberg - Putzenfeld | Dürrnberg - Eislfeld | Dürrnberg - Eislfeld | Dürrnberg - Lettenbühel | Langenau

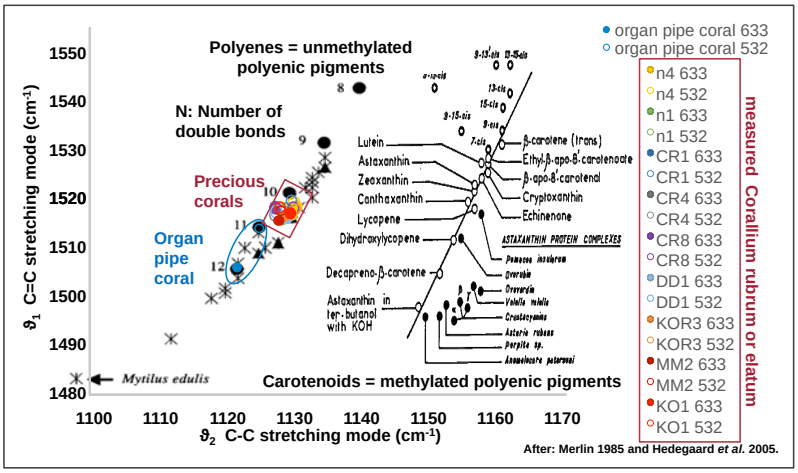
Pure Calcite without Polyenes

Hänichen | Kleinkorbetha

Pearls of inorganic origin

Dürrnberg - Römersteig Cuprite | Dürrnberg-Putzenkopf Cuprite | Dürrnberg - Moserstein Kaolinite, Quartz

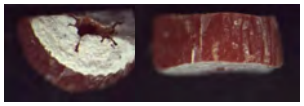




After: Merlin 1985 and Hedegaard *et al.* 2005.

Results and Discussion:

Corallium Rubrum

Original	200°C	$(Na,NH_4)_2SO_4$ + HCL	$KMnO_4$	H_2S_x
				
Mg-Calcite Polyenes $N_{eff.}$ ~ 10	Mg-Calcite stable, Polyene decay	Red rim: Gypsum and Polyenes White core: Calcite, Gypsum and Polyenes	Aragonite + (Mn(Ca),Mg)OOH	Cc + Aragonite

Organ Pipe Coral

Original	200°C / NaOH + 100°C
	
Mg-Calcite Polyenes $N_{eff.}$ 11 - 12	Thermonatrite, Portlandite

Chemical treatment revealed inorganic material decays (transformation of Calcite to Gypsum, Thermonatrite and Portlandite or Aragonite. Only red corals treated at high temperature (here: 200°C) and in concentrated NaOH showed discoloration, due to Polyene degradation.

None of the experiments lead to bleaching with a preservation of Calcite or without decay of Polyenes. Consequently, post mortem bleaching of red corals can be excluded. In contradiction to the archaeologicaly suggested bleaching of red corals, either intended or during ground exposure, the hypothesis of primary white corals is proposed.