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Bitterfeld amber is not Baltic amber: Three geochemical tests and further constraints on the botanical affinities of succinite

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ABSTRACT

Baltic and Bitterfeld ambers are important deposits of polymerized conifer resin that are widely recognized for their exquisite fossil inclusions, especially insects. Because of over-arching similarities with respect to visual appearance, organic geochemistry, arthropod assemblages, and proximity to forests of the Paleogene North Sea margin, these two ambers have not yet been differentiated definitively, leading to ongoing debate as to whether or not they (and their respective inclusions) are truly equivalent. We combine micro-Fourier transform infrared spectroscopy (FTIR), time of flight-secondary ion mass spectrometry (ToF-SIMS), and stable isotopes ($\delta^{13}C$ and $\delta^{2}H$) to establish that Baltic and Bitterfeld ambers differ consistently in their geochemical properties, and thus capture distinct depositional episodes in space, but not necessarily in time. Baltic amber has more succinic acid, succinic anhydride, and communic acid relative to Bitterfeld amber, but less dehydroabietic acid. Although both ambers produce overlapping $\delta^{13}C$ values, supporting a similar age of formation, $\delta^{2}H$ is markedly depleted (by ~20‰) in Baltic amber relative to Bitterfeld amber. The hydrogen isotopic results confer paleolatitudinal differences in amber provenance, that is, a clear differentiation between sources originating from the northern (Baltic) and southern (Bitterfeld) margins of the Paleogene North Sea. We conclude that the two deposits are geologically distinct in origin, but that similarities in their respective faunal records arise because they are broadly coeval in time. We also present new ToF-SIMS results that imply only resins from modern conifers of the families Pinaceae and Sciadopityaceae begin to satisfy the expanded geochemical profiles presented for Baltic and Bitterfeld ambers.

1. Introduction

Baltic amber is the world's best known deposit of fossil plant resin, and by far the single largest repository of fossil insects of any age (Weitschat and Wichard, 2002, 2010). Unlike in situ fossil resins that are directly associated with lignite, coal, or other plant-rich strata, Baltic amber is a secondary deposit found mainly in glauconitic marine sediments of middle Eocene age (Lutetian Stage; 41.3–47.8 Ma), deposited along the paleo-North Sea margin. The blue earth (or Blaue Erde) in which Baltic amber is principally hosted occurs in Russia (Kaliningrad Oblast), Poland, and Germany, but detrital Baltic amber, redeposited by Quaternary glacial and fluvial processes, reaches Scandinavia, the Baltic republics, and the British isles. Baltic amber has been exploited for millennia, and is widely disseminated in European archaeological contexts (Beck et al., 1965). The botanical origin of Baltic amber is a topic of intense scrutiny and longstanding debate, for which the only firm conclusion is that source trees were extinct conifers (Mills et al., 1984; Mosini and Samperi, 1985; Wolfe et al., 2009; Dolezych et al., 2011).

Bitterfeld amber originates from a much more restricted geographical area, the silts and sands, or "Bernsteinschluff", of the Cottbus Formation near the town of Bitterfeld in Upper Saxony (Sachsen-Anhalt; hence the synonym Saxonian amber). Although once assigned a Miocene age (Barthel and Hetzer, 1982), more recent geochronological efforts (Knuth et al., 2002) place these sediments in the late Oligocene (Chattian; 23.0–28.1 Ma). As with Baltic amber, Bitterfeld amber is a secondary deposit that preserves an exceptional record of fossil arthropods. Bitterfeld amber was actively mined at the site of Goitzsche between 1975–1993, yielding a gem quality resource and thousands of arthropod inclusions (Dunlop, 2010). Careful geological mapping of the Bitterfeld amber complex shows that amber is concentrated in low-energy lagoonal facies associated with a deltaic system discharging into the North Sea from the south (Wimmer et al., 2006; Fuhrmann, 2008).

Bitterfeld amber is similar to Baltic amber with respect to hardness and visual appearance (Fig. 1), the ubiquitous presence of succinic acid (both are referred to as succinites; Anderson and Botto, 1993), several elements of their respective arthropod assemblages, and the

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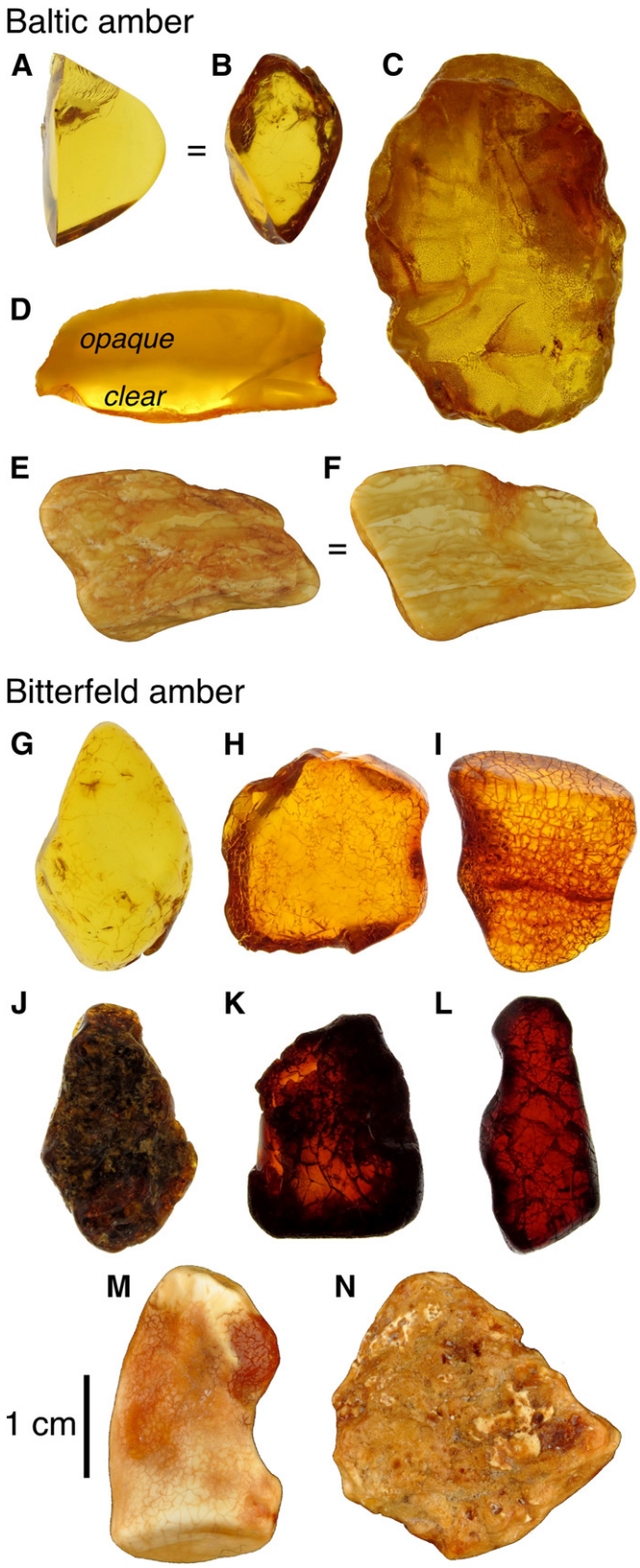

Fig. 1. Photographs of Baltic (A–F) and Bitterfeld (G–N) amber specimens. Polished (A–B) and unpolished (C) clear Baltic ambers ("honey"), the latter with surface desiccation cracks. (D) Internal zonation between clear and partially opaque "butterscotch" ambers. (E–F) Outer and internal views of completely opaque "bone" amber with multiple generations of flow lines, or schlaube. (G–L) Bitterfeld amber ranging from clear yellow to dark reddish-brown. The dark nearly specimen (M) is classified as "glessite", the name given to this variant, which occurs in both Baltic and Bitterfeld deposits. (M–N) Bitterfeld bone amber.

generalized geography of European amber distribution. For this reason, some have argued that they are necessarily coeval, Bitterfeld amber being merely a younger redeposited fraction of primary Eocene Baltic amber. In this model, both ambers share a common botanical origin. This view is supported by similarities between the faunal inclusions of both deposits with respect to Arachnida (harvestmen: Dunlop and Mitov, 2009; spiders: Wunderlich, 1993, 2004), Coleoptera (dermestids: Háva and Alekseev, 2015); Diptera (acalyptrates: von Tschirnhaus and Hoffeins, 2009; anthomyzids: Roháček, 2013; ceratopogonids: Szadziewski, 1993; Sontag and Szadziewski, 2001; limoniids: Kopeć and Kania, 2013; nymphomyiids: Wagner et al., 2000), and Hymenoptera (apoid bees: Engel, 2001; and wasps: Ohl and Bennett, 2009). Indeed, the viewpoint that Baltic and Bitterfeld ambers have an identical provenance is held strongly, and has been particularly well articulated by Weitschat (2008, pp. 94), whose translated statement reads:

> "Northern European amber production began during warm conditions of the early Eocene, and terminated by the end of the middle Eocene. The cooling trend over this interval resulted in irreversible changes in the flora and fauna of northern Europe: tropical and subtropical elements were progressively replaced by boreal 'arcto-Tertiary' assemblages. The amber forests recorded this transition, given that Baltic and Bitterfeld deposits both contain taxa belonging to tropical as well as boreal ecotypes, at times the very same species. The case is especially convincing with regard to spiders, suggesting that Baltic and Bitterfeld ambers both originated from a single forest ecosystem in western Scandinavia, which persisted for up to 10 million years under a sustained warm climate regime."

More recently, even stronger statements to the same effect have been issued from the paleoentomological community (Szwedo and Sontag, 2013, pp. 380):

> "At present, there is no doubt that amber from Bitterfeld (Saxonian amber) is contemporaneous with Baltic amber, i.e. that it originated in the Eocene and that it belongs to the Baltic amber group."

However, a balanced and thorough review of the subject (Dunlop, 2010) leaves unresolved the question as to whether Baltic and Bitterfeld ambers are truly identical in age and origin. Arguments based on stratigraphy (Knuth et al., 2002) and organic geochemistry (Yamamoto et al., 2006) challenge the view that Baltic and Bitterfeld ambers are equivalent, as do paleobiological studies that nuance the rate and tempo of evolutionary processes among and between organismal groups (Barthel and Hetzer, 1982; Dunlop and Giribet, 2003; Schmidt and Dörfeldt, 2007; Dlussky and Rasnitsyn, 2009). The resolution of this dilemma constitutes the impetus for the present study, in the footsteps of important yet inconclusive regional symposia on this exact topic (Ganzelewski et al., 1997; Rascher et al., 2008). We report results from three parallel suites of geochemical analyses that bear directly on the differences and similarities between Baltic and Bitterfeld ambers, and conclude that they are compositionally distinct from each other and do not share the same geographical provenance, while remaining largely contemporaneous in their age of formation.

2. Materials and methods

Samples of Baltic and Bitterfeld ambers have been collected, purchased, and obtained through exchange with colleagues. A sizeable collection of Baltic amber specimens from Germany, Lithuania, Poland, Russia, and southern Sweden was amassed during previous investigations (Wolfe et al., 2009). Baltic amber specimens were sub-sampled from this collection for the geochemical analyses described below. Bitterfeld amber specimens include samples confirmed to originate from the Goitzsche mine and offered for study by Alexander Schmidt