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Calculation of the conodont Color Alteration Index (CAI) for complex thermal histories

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ABSTRACT

A simple model for the Arrhenius reaction conodont Color Alteration Index (CAI) that can be implemented easily in a computer program is introduced. The model, named to as EasyCAI, envisages the overall process of conodont alteration as a series of 12 parallel pseudo-first-order reactions. Our approach is especially amenable to a spreadsheet program and can solve complex geological histories involving variable heating and cooling rates. With EasyCAI, a profile of CAI values versus time can be obtained for a given stratigraphic level if the time–temperature history for that level has been estimated. EasyCAI can provide additional constraints to optimize thermal history models by computing profiles of CAI values with depth and time; thus providing a new tool for quantitative CAI palaeothermometric analysis.

1. Introduction

Conodonts are tiny (0.2 to 2 mm) apatitic remains of the feeding apparatus of an extinct animal group of the Class Conodonta, which was common in Cambrian to late Triassic oceans. These tooth-like microfossils have become a widely used tool in integrated basin analysis and hydrocarbon exploration because of its coupled use as precise biostratigraphic markers and thermal maturity indicators. The latter property is based on the analysis of color that changes as the conodont elements experience progressive and irreversible chemical transformations of the organic matter interspersed within the hyaline crown tissues (Marshall et al., 2001; Trotter et al., 2007) as a response to increasing temperature with time. The conodont color change has long been known (Ellison, 1944) but it has not been explained and quantified until the works of Epstein et al. (1977) and Rejebian et al. (1987), who established the conodont Color Alteration Index (CAI) and calibrated their values according to heat and exposure time, in accordance with the Arrhenius reactions.

The CAI method is an easy and inexpensive procedure, and is specially suited for Palaeozoic carbonate rocks, where other thermal maturity indices, such as the coal rank, vitrinite reflectance and Thermal Alteration Index (TAI), fail due to their biostratigraphic span, inadequate lithology, or their effective temperature range. Palaeotemperature data derived from CAI values are frequently employed in basin analysis, metamorphic studies, and in determining thermal aureoles related to short-term heating events (e.g., Kovács and Árkai, 1987; Nowlan and Barnes, 1987; Burnett, 1987, 1988, Rasmussen and Smith, 2001; Wiederer et al., 2002; Zhang and Barnes, 2007; Voldman et al., 2009). However, the CAI method is based on the assumption that heating events take place at constant temperature, which can conduct to inaccurate interpretations of palaeotemperatures or geothermal palaeogradients, particularly when dealing with complex and prolonged thermal histories. An accessible solution to this problem is proposed in this paper.

2. The conodont Color Alteration Index (CAI)

Conventionally, CAI values are determined under incident light on the outer basal margins and finest sections of the conodont elements by direct comparison with a set of laboratory produced standards or with the Munsell soil color chart (Epstein et al., 1977). Unaltered conodonts present a pale yellow and a smooth surface with silky brightness (CAI 1). Gradually increasing temperature results in successive carbonization processes of conodont elements that outcome in the color sequence light through dark brown (CAI 1.5–4) to black (CAI 5). Subsequent color changes towards grey (CAI 6), white (CAI 7) and finally translucent (CAI 8) are consequences of oxidation of organic matter, release of constitutional water and recrystallization. Epstein et al. (1977) and Rejebian et al. (1987) calibrated the different CAI stages, ranging in temperature from 50 to >600 °C, by means of laboratory experiments and extrapolated their experimental data to geologic time scales through the Arrhenius plot (Fig. 1). From these pioneer works, much research has been accomplished in order to quantify the conodont color alteration index, employing electron spin

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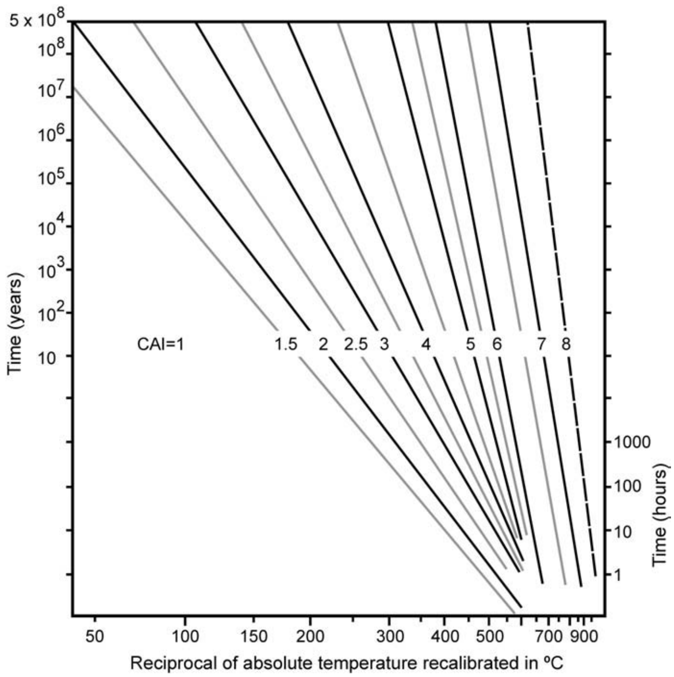

Fig. 1. Arrhenius plot of fields of CAI 1 through 8 from Epstein et al. (1977) and Rejebian et al. (1987). The gray curves are intermediate CAI values, usually discernable under the binocular microscope. Each CAI curve represents all combinations of temperature and time (isothermal conditions) that result in the corresponding CAI value.

resonance (Belka et al., 1987), organic geochemistry (Bustin et al., 1992; Marshall et al., 1999), spectral reflectance (Deaton et al., 1996), and color image analysis (Helsen et al., 1995; Bábek et al., 2008), among other techniques, with varying degrees of certainty. A general correlation between illite crystallinity and CAI values determined that the CAI range from 4 to 5.5 reflects anchizone boundaries.

The conodont color alteration sequence follows the Arrhenius reaction, therefore it is progressive, cumulative and irreversible. Short-term heating events do not necessarily produce the normal gradational conodont color alteration sequence. Usually, contact metamorphosed conodont elements have a broader range of CAI values, both locally from sample to sample and even within same sample. Moreover, contact metamorphosed conodonts are generally not deformed but strongly recrystallized: the size of single crystals on conodont elements suggests a close relationship between the growth of apatite crystals and the determined CAI value (Burnett, 1988; Königshof, 1992). Conodont elements recovered from hydrothermally altered rocks may show similar CAI distributions, but they are generally corroded and present a superficial grey patina (Rejebian et al., 1987). Under these circumstances, CAI values from 6 to 8 can be misleading in assessing temperatures, as the conodont color could result equally from oxidation of organic matter or from the temperature range experienced by the host rock during hydrothermal activity.

Besides thermal maturation, other factors such as dolomitization and diagenesis that could affect the CAI are usually accompanied by indicative textural alterations of the conodont surfaces, like patinas or coarse recrystallization (e.g., Burnett, 1988; Königshof, 2003; Voldman et al., 2008). Alternatively, robust conodont elements are usually darker, but this aspect has limited significance if similar forms are consistently selected for the color analysis. The influence of tectonics on CAI values is directly related to the variation of overburden levels, making it possible to use conodonts as geothermometers within orogenic belts (e.g., Rasmussen and Smith, 2001), though the combination of water and confining pressures may eventually lead to CAI suppression by inhibiting the charring processes, as it is observed in overpressured rocks (Epstein et al., 1977; cf. Hao et al. 2007). This mechanism is also invoked to explain oil production at anomalously high temperatures within overpressured systems, where the organic matter maturation has been retarded. Under increasing conditions of regional dynamothermal metamorphism, where besides temperature, fluid pressure and oriented stress can play significant roles, recrystallization and ductile deformation of conodonts could be accelerated, in accordance with the metamorphism and ductile deformation experienced by the host rock (Teichmüller, 1987; Sudar and Kovács, 2006). Ultimately, the CAI can be influenced by the composition of the host-rock due to infiltering of hydrocarbons or pyrite in the laminated conodont structure under reducing conditions or by enhanced thermal maturation related to radioactive decay of uranium (e.g., Helsen, 1997). This phenomenon usually represents less than 0.5 CAI units and can be avoided by working with similar lithologic types, especially with unweathered calcareous rocks.

CAI values caused by thermal alteration (e.g., sedimentary burial or contact metamorphism) can be predicted from a time–temperature Arrhenius graph, which shows the resulting CAI values produced after heating a conodont sample at constant temperature for a given period of time (Epstein et al., 1977; Rejebian et al., 1987). However, the application of this plot to complex geological histories is difficult because under natural conditions the heating occurs at variable temperatures, hampering the precise determination of palaeotemperatures or geothermal palaeogradients from CAI data. To overcome this problem, García López et al. (2001) proposed a graphic solution to estimate reliable palaeogradients from CAI data if the mean sedimentation rates and the chronostratigraphic boundaries of the units are known. Nevertheless, their method has some limits: (1) it evaluates the time the rock was above a specific temperature, despite the fact that CAI depends on the integral of temperature with time, (2) it assumes that the heating time is equal to the cooling time, oversimplifying the burial history, and (3) it is rather difficult to implement in a computer program. Herein, we present a simple model for the Arrhenius reaction of the conodont color alteration index (CAI), named to as EasyCAI, that overcomes all of these problems.

3. CAI calculations for complex thermal histories with variable heating rates

We assume that the chemical reactions considered here can be described by a pseudo-first order law,

$$dw/dt = -kw, \tag{1}$$

where w is the reactant concentration and k is the pseudo-first order reaction rate constant. The temperature dependence of k is expressed by the Arrhenius equation:

$$k = A\exp(-E_a/RT), \tag{2}$$

where E_a is the activation energy, A the pre-exponential factor, T the temperature and R the universal gas constant. Inserting this equation into Eq. (1) and solving it for constant T gives:

$$w = w_0 \exp\left(-Ae^{(-Ea/RT)}t\right) \tag{3}$$

We assume a linear dependence of the transformation ratio F of the reaction (ranging between 0 and 1) with CAI,

$$CAI = CAI_{\min} + w_F F \tag{4}$$

were $F = 1 - w/w_0$ and w_F is a constant weight factor. Combining Eqs. (3) and (4) results in:

$$CAI = CAI_{\min} + w_F\left[1 - \exp\left(-Ae^{(-Ea/RT)}t\right)\right], \tag{5}$$