

Geochemical study of stable carbon and oxygen isotopes in landfilled Ca-rich oil shale ash

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Abstract. The Estonian energy industry relies on local calcareous oil shale that is used to produce the majority of the country's electricity, but the shale is also used for shale oil retorting. The solid residues remaining after combustion are upon open air deposition potentially capable of binding part of the released CO₂ by carbonation of reactive Ca-phases. We studied the isotopic composition of authigenic carbonate phases in an alkaline Ca-rich oil shale ash waste deposit accumulated over nearly 50 years to reveal the carbonation mechanisms and the sources of CO₂ required for carbonation. The secondary carbonate phases forming in oil shale waste deposits have low δ¹³C and δ¹⁸O values characterized by δ¹³C_{V-PDB} values between –12‰ and –24‰ and δ¹⁸O_{V-PDB} between –8‰ and –15‰. The negative isotopic composition of carbonate carbon seemingly points to a contribution of CO₂ derived from the degradation of residual organic material, potentially present in shale retorting ashes. The low δ¹³C value of carbonate is rather caused by the non-equilibrium fractionation effects during diffusion and hydroxylation reactions of CO₂ in hyperalkaline conditions under a limited CO₂ diffusion rate.

Key words: oil shale ash, stable isotopes, carbon, oxygen, carbonation.

INTRODUCTION

Estonia is among a few countries where kerogenous oil shales are used for power generation and shale oil retorting (Koel 1999). Oil shales are of varying organic matter content and typically have low calorific value and high ash content. The oil shale mined and processed in Estonia – the Ordovician kukersite oil shale – is particularly characterized by a high Ca content because the oil shale seams occur in a normal marine carbonate succession (Bauert & Kattai 1997). Currently *ca* 15 million tonnes (Mt) of calcareous oil shale is mined and about 6–8 Mt of alkaline Ca-rich ash waste is produced annually in Estonia. Only a few per cent of the ash is reused, mainly in cement production and in agriculture as a liming agent. The rest becomes hydraulically deposited into large waste depositories occupying a more than 20 km² area next to power plants and/or oil retorting plants (Mõtlep et al. 2010; Konist et al. 2016).

Historically pulverized combustion (PC) firing has been used at Estonian oil shale power plants where

combustion temperatures in the boiler reach 1350–1400 °C (Konist et al. 2013). In circulating fluidized bed combustion (CFBC) boilers, currently in use at the oil shale firing Estonian power plants, the combustion temperatures are in the range of 800–850 °C (Hotta et al. 2005), allowing complete burn-off of organics but only partial thermal dissociation of dolomite and calcite – carbonate minerals dominant in oil shale. Dolomite decomposition into CaO, MgO and CO₂ begins at *ca* 550 °C whereas calcite decomposition, which produces most of the CaO and CO₂, starts at *ca* 620 °C and reaches a maximal rate at 895–900 °C (L'vov 2007). During shale oil retorting in solid heat carrier (SHC) retorting processes the temperatures are kept lower, in the range of 400–500 °C. The spent shale that still contains a considerable amount of residual organics is burnt at 700–800 °C for a short time before it is reintroduced as a heat carrier into the retort (Kann et al. 2004; Sedman et al. 2012). The solid residues from the older SHC technology (e.g., Enefit140 and Petroter) still contain up to 2–3% of residual organics because of the incomplete burn-off of the solid residues

(Talviste et al. 2013). In contrast, in the most modern shale oil retorting plant (Enefit280, commissioned in 2012) where the SHC retort is combined with a CFBC unit the final ash is virtually free of organic residues (Paaver et al. 2017; Neshumayev et al. 2019).

As a result of carbonate decomposition processes during the combustion in electricity production and also in the final steps of retorting, the ash remaining at power plants is rich in reactive free CaO and MgO (Kuusik et al. 2005; Bityukova et al. 2010; Mõtlep et al. 2010). Due to the high reactivity, the initial reactions (hydration of alkali oxide phases) start during the hydraulic transportation of ash to the depositories and continue with more complex transformation reactions in the ash deposits that proceed over decades (Mõtlep et al. 2010; Leben et al. 2019; Pihu et al. 2019). Aging of the ash containing free CaO and MgO, also known as quick lime and periclase, is mainly governed by carbonation in open air conditions (Liira et al. 2009). These reactions proceed through the hydration of CaO to Ca(OH)₂ (portlandite) which further reacts with the (atmospheric) CO₂ to form a stable calcium carbonate (CaCO₃) phase. An important aspect of the carbonation is the neutralization of the ash material that, at the initial hydration step, has a pH of 12–13 controlled by portlandite equilibrium. With progressing carbonation pH gradually decreases to ~8, reaching equilibrium with calcite. Leben et al. (2019) have recently shown that in oil shale ash deposits, the long-term ash transformation is more complex than a simple carbonation reaction. Under highly alkaline conditions the Ca-rich ash is transformed into different calcium silicate hydrate (C-S-H) phases, where carbonation is subdued, probably because of limited diffusion of atmospheric CO₂ into the consolidated and cemented ash deposits.

In this paper we study the stable isotope composition of the authigenic calcite in the nearly 40 m thick ash deposit at Eesti Power Plant that has been accumulated over 50 years. In this depository the ash from power plants has been mixed with the ash from oil retorting plants containing residual organic material. It is commonly assumed that atmospheric CO₂ is the source of carbon dioxide during the open-air carbonation (Uibu et al. 2008; Konist et al. 2016).

If organic carbon is present in ash material, it can be used up by chemoheterotrophic microorganisms degrading the residual organic matter and producing additional CO₂ within the sediments themselves (Chan 2003). This CO₂ can be used by carbonation reactions within ash deposits. Microbial study of oil shale ash deposits has shown that saprotrophic bacterial and fungal taxa common to mine spoils throughout Europe are dominant among the primary colonizers of oil shale ash sediments (Cowden & Shefferson 2011). Also, because oil shale ash is rich in anhydrite, a Ca-sulphate mineral (Bityukova et al. 2010),

the water draining off the ash plateaus has a high dissolved sulphate content. This makes a favourable environment for sulphate-reducing microorganisms that are also capable of biodegradation of residual organics and production of CO₂ with a $\delta^{13}\text{C}$ value lower than atmospheric CO₂. The aim of this contribution is to reveal the main source of CO₂ in carbonation reactions in oil shale ash deposits and to what extent the biologically produced CO₂ could be involved in carbonation.

MATERIALS AND METHODS

The ash samples were taken from a drill core made on the rim of the ash disposal site at Eesti Power Plant, northeastern Estonia (Fig. 1). The total thickness of the deposit at the drilling site was 37.5 m. The groundwater level in the drill hole was measured at a depth of 6.6 m below surface. The Eesti Power Plant was commissioned in 1969 and the ash depository has been in use since then. Along with oil shale PC ashes, the oil retorting ashes from SHC retorts have been co-deposited with the oil shale combustion ash since the 1980s. Also, ash from CFBC has been deposited since the year 2004, contributing to the sediments in the upper few metres of the section.

The mineralogy and chemical composition of the ash deposit analysed by X-ray diffraction and X-ray fluorescence, respectively, was reported in Leben et al. (2019). In this study the C and O isotopic composition of 19 ash sediment bulk samples was analysed.

Additionally, an experimental laboratory study of oil shale ash carbonation was undertaken to investigate the initial rapid changes in the carbonate isotope composition of bulk ash sediments over time. During the experiment the fresh fly ash from the electrostatic precipitators of the CFBC boiler at Balti Power Plant was fully hydrated and stored in open air conditions. Dried ash bulk samples were taken for isotope analysis after two weeks and three months of curing.

The share of the retorting ash in the total ash sampled in the depository at Eesti Power Plant is unknown but its relative contribution (absent, low, medium, high) was estimated in the studied samples by the sediment colour (see the supplementary data table online at <https://doi.org/10.15152/GEO.491>). The hydrated ash from power plants is white to pale beige-grey whereas the ash from SHC retorts is dark-grey to black. The Munsell colour system codes were used for colour definition in 70 samples covering the full section of the deposits and three samples from the base of the ash deposit. The representation of the Munsell colour codes was converted into digital approximations in the sRGB colour system (Centore 2013; Geng 2015).



Fig. 1. Location of the ash waste deposit.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonates in ash sediment samples were measured using the Thermo Delta V Advantage continuous flow isotope ratio mass spectrometer. An analytical precision (2σ) of 0.1‰ was determined by repeated analyses of a standard. The dried bulk ash samples were dissolved in 99% H_3PO_4 and the resulting CO_2 gas was analysed by the spectrometer. The measured isotopic composition is presented as delta notation (δ) in relation to the Vienna Pee Dee Belemnite (V-PDB) standard and expressed in per mil (‰). Delta notation is defined as $\delta = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}] \times 1000$, where R is the stable isotope ratio of $^{13}\text{C}/^{12}\text{C}$ or $^{18}\text{O}/^{16}\text{O}$.

The equilibrium temperature of carbonate precipitation was calculated according to Hays & Grossman (1991) and Grossman (2012) using equation (1):

$$T = 15.7 - 4.36(\delta^{18}\text{O}_{\text{cal}} - \delta^{18}\text{O}_{\text{water}}) + 0.12(\delta^{18}\text{O}_{\text{cal}} - \delta^{18}\text{O}_{\text{water}})^2, \quad (1)$$

where the $\delta^{18}\text{O}_{\text{cal}}$ values correspond to the measured oxygen isotopic composition of calcite relative to V-PDB and $\delta^{18}\text{O}_{\text{water}}$ is the monthly weighted mean Estonian rainfall oxygen isotopic composition of -10.4‰ for the years 1982–1985 relative to V-SMOW (Vienna Standard Mean Ocean Water) from Punning et al. (1987). This period corresponds to the peak in oil shale mining and hence ash generation. More recently Stansell et al. (2017) have suggested an average total annual precipitation weighted value of -10.3‰ $\delta^{18}\text{O}_{\text{V-SMOW}}$ but this causes only a minute variation in calculated values.

RESULTS AND DISCUSSION

Sediment characteristics

The colour of the sediments in the studied section varies from white-pale grey (Gley 1 9/N) to dark grey (Gley 1 4/N) (supplementary data table online at <https://doi.org/10.15152/GEO.491>). Darker layers correspond to a higher share of oil retorting ash in the given layer. The darkest layers with the highest estimated oil retorting ash content occur in the uppermost 2 m and at around 12 m depth. Layers with an estimated medium to low oil retort ash content are located at around 7–9, 13–18 and 22 m. The lowest darker layers occur between 25 and 28 m depths, likely indicating the period around the first deposition of oil retorting ash on the deposit in the 1980s. Layers of lighter-coloured ash with no apparent oil retorting ash content make up the most of the deposit, occurring around 2–7, 9–12, 17–21 and 22–25 m depths; and from 28 m onwards to the bottom of the deposit at 38 m depth. The very bottom of the ash deposit can be drawn above the brown-coloured (code 10 YR 5/3) compressed peat layer and the sand- and clay-rich layers below it.

The chemical composition of the ash sediment dominated by SiO_2 , CaO and Al_2O_3 is rather uniform (see Leben et al. 2019). The carbonate composition of the ash sediment samples was dominated by calcite with values up to 25.5%. Additionally, minor amounts of vaterite ($\gamma\text{-CaCO}_3$ polymorph) up to 1.5% were detected. Although the mineral composition varies considerably throughout the section, these variations reflect the diagenetic conditions of the mineral recrystallization (Mötle et al.

2010; Leben et al. 2019) rather than variation in initial ash sediment composition. The composition of Enefit140 SHC retorting ash formed at oil retorting plants next to Eesti Power Plant is poorly known because the ash cannot be extracted from the retort units in a dry state. However, the technology used at these retorts is similar to that of Petroter SHC retorts and the composition of dark grey to black ash forming at Petroter in principal is similar to the fly ash produced in CFBC boilers at power plants. The most notable difference is the presence of the Ca-sulphide phase (CaS – oldhamite) in oil retorting ash instead of Ca-sulphate (anhydrite) occurring in CFBC ash (Sedman et al. 2012; Talviste et al. 2013). CaS is, however, unstable under atmospheric conditions and quickly becomes dissolved and oxidized into sulphate (Kann et al. 2004). Therefore, given the similar composition of the retorting and power plant ashes, the compositional variation with respect to the estimated share of the retorting ash to the total ash in ash sediment is not expected.

Some covariation between sample colour and mineral composition was reported by Leben et al. (2019). In general, grey-coloured samples with a higher estimated oil retorting ash content also display a higher terrigenous mineral content and pale beige-coloured combustion ash layers correspond to an elevated secondary Ca-mineral (portlandite) content. However, a clear correlation between sample colouration and mineral or chemical composition could not be established.

Carbon and oxygen isotope composition

All analysed sediment samples show negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values relative to the V-PDB scale (Table 1; Fig. 2). The $\delta^{13}\text{C}$ values varied from -11.9‰ to -22.9‰ for ash waste deposit samples and $\delta^{13}\text{C}$ values in laboratory experiment samples were -23.2‰ and -24.3‰ after two weeks and three months, respectively. The $\delta^{18}\text{O}$ values varied between -7.9‰ and -15.1‰ for the waste deposit sediments, and -12.0‰ and -14.2‰ for laboratory experiment samples after two weeks and three months, respectively. There is no clear statistically significant correlation between C- and O-isotope values (Fig. 2).

The measured $\delta^{13}\text{C}$ value of carbonates formed in the ash sediment is relatively low. The carbonate (calcite) precipitating in equilibrium with atmospheric CO_2 should have a $\delta^{13}\text{C}$ value of around 0‰ . Present-day $\delta^{13}\text{C}$ values of atmospheric CO_2 shifted from *ca* -7.5‰ in the late 1970s to -8.3‰ by 2015 (Keeling et al. 2017), which would result in a shift of about -1‰ to carbonate $\delta^{13}\text{C}$ values. Typically, negative stable carbon isotope values are considered to signal the involvement of CO_2 of organic origin, for example, due to microbial activity (Whiticar 1999; Campbell et al. 2003). In this sense the strongly ^{13}C depleted carbonate isotope values in the ash

Table 1. Stable isotope composition and the calculated equilibrium temperatures of ash sediments. Experimental cemented ash samples – Exp(hardening time, weeks/months)

Depth (m)	$\delta^{13}\text{C}_{\text{V-PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{V-PDB}}$ (‰)	Temperature (°C)
0.45	-11.95	-9.13	10.36
1.85	-19.55	-11.39	20.13
3.55	-17.11	-12.12	23.55
5.70	-18.92	-12.95	27.60
7.85	-14.25	-10.58	16.49
9.80	-16.56	-11.21	19.31
11.90	-14.23	-8.88	9.35
13.85	-16.85	-7.95	5.74
16.05	-16.32	-8.78	8.95
17.95	-18.40	-15.06	38.62
20.00	-16.84	-11.78	21.95
22.40	-16.32	-10.24	15.01
24.85	-18.90	-11.73	21.71
27.00	-17.43	-10.39	15.66
29.05	-22.95	-10.76	17.29
31.05	-15.16	-8.94	9.59
33.00	-15.93	-9.16	10.48
34.95	-17.81	-10.26	15.09
38.25	-21.17	-9.85	13.34
Exp(2 w)	-23.24	-14.16	33.77
Exp(3 m)	-24.28	-11.96	22.77

depository at Eesti Power Plant seemingly point to the involvement of CO_2 derived from bacterial degradation of some residual organics. Considering the atmospheric industrial period $\delta^{13}\text{C}$ value of around -8‰ , with an equilibrium fractionation between atmospheric CO_2 and calcite of $+9.6\text{‰}$ (Emrich et al. 1970), and CO_2 derived from the degradation of organic matter, $\delta^{13}\text{C}$ with a value of *ca* -30‰ would lead to the approximate measured values in this case. By assuming a simple mixing and mass-balance between these two CO_2 reservoirs, the oil shale ash carbonate $\delta^{13}\text{C}$ values varying from -11.9‰ to -22.9‰ would denote the contribution of organics-derived light CO_2 to the total CO_2 pool in the range of 50–90%.

However, the carbonate isotope fractionation in natural environments is also sensitive to the pH of the environment where carbonate minerals are precipitated because of pH dependence on isotope fractionation between carbon species (e.g., Swart 2015). The correlation between carbon isotope composition and the varying pH in precipitating calcite has previously been brought out by

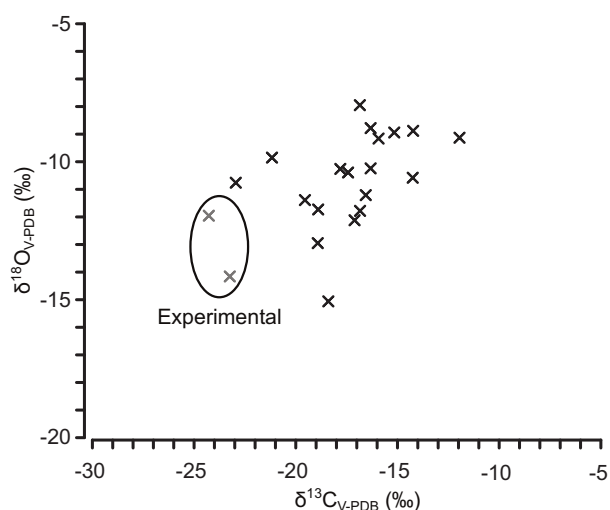


Fig. 2. Carbon and oxygen stable isotope composition of ash sediments.

Dietzel et al. (1992), showing that carbonate precipitated at higher pH has a more negative isotopic composition than the calcite precipitated under neutral pH conditions.

The diagenetic transformation of Ca-rich ash sediments in highly alkaline conditions can be compared to past and present natural alkaline environments where negative stable carbon isotope fractionation in authigenic carbonate phases has been described (e.g., Arp et al. 2013, 2016; Leleu et al. 2016). Nevertheless, in most cases the natural highly alkaline water bodies are soda lakes (for example Lake Bogoria, Lonar Lake, Mono Lake and others), which have a comparatively low Ca^{2+} and Mg^{2+} content and the main carbonate minerals forming in these environments are usually Na-based (Grant 2006). Carbonate precipitation rates in these lakes are very low and associated with high evaporation and low outflow rates that ensure a stable high pH and often elevated salinity, whereas the $\delta^{13}\text{C}$ values of Na-carbonates forming in these lakes can be positive (Grant 2006; Anoop et al. 2013).

There are alkaline water bodies, often related to hydrothermal activity, where the cation composition of alkaline water is dominated by dissolved Ca and Mg species. These water bodies are more similar to oil shale ash plateau environments and processes. Comparison to natural alkaline environment can be done in a former lake basin inside the Ries meteorite crater in southern Germany, formed 14.59 ± 0.20 Ma ago (Buchner et al. 2010). After the impact the crater depression was filled with an isolated lake where lacustrine sediments accumulated over a long period of time during different stages of lake development with highly varying environmental conditions, resulting in carbonate

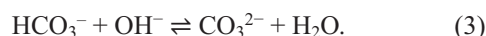
sediments with a wide range of isotopic compositions (Arp et al. 2013). However, $\delta^{13}\text{C}$ values of carbonate precipitates in this alkaline lake and associated hot water spring travertine deposits (and hydrothermal vein calcite) are in the range of +4‰ to –8‰ (Arp et al. 2016); these are far higher isotopic values than $\delta^{13}\text{C}$ values of –14‰ to –23‰ recorded in the oil shale ash deposit.

The low $\delta^{13}\text{C}$ values seen in this study are more similar to those in travertines formed in hyperalkaline springs in the Oman ophiolite massif (Clark et al. 1992; Leleu et al. 2016). The Oman system is characterized by Ca-rich highly alkaline groundwaters (pH up to 11.9) where carbonate deposits have $\delta^{13}\text{C}$ values as low as –22.8‰. In this setting the Ca-OH-type hyperalkaline groundwater depleted in dissolved inorganic carbon (DIC) and enriched in Ca leads to fast precipitation of calcite when mixing with inorganic carbon-rich surface water and on diffusion of atmospheric CO_2 (Clark et al. 1992).

Under hyperalkaline conditions the carbonate system is far from equilibrium and highly negative non-equilibrium fractionation of stable isotopes in carbonates is controlled by aqueous kinetic effects during hydroxylation of CO_2 (Clark et al. 1992). Clark et al. (1992) suggested that diffusion of atmospheric CO_2 occurs rapidly with respect to aqueous reactions and reaches equilibrium conditions between aqueous and gaseous CO_2 with the enrichment factor of 1‰ for ^{13}C in $\text{CO}_{2(\text{aq})}$. They concluded that a significant 15.56‰ depletion of $\delta^{13}\text{C}$ values in the carbonate phases precipitating in alkaline conditions is the result of the lower activation energy of ^{12}C –O bonding (compared to ^{13}C –O) on the hydroxylation reaction of $\text{CO}_{2(\text{aq})}$ with OH^- producing HCO_3^- (equation 2):



Bicarbonate becomes hydrolysed to CO_3^{2-} in alkaline conditions (equation 3), which is the dominant species at high pH above 10 (associated with depletion of ca –0.4‰ with respect the ^{13}C at 25 °C):



On the other hand, Dietzel et al. (1992) have suggested that the reported depletions in ^{13}C of carbonates are due to kinetic effects additionally caused by the different diffusion rates of gaseous $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ as well as the hydroxylation rates of dissolved aqueous CO_2 . The latter view was also supported by the study of Leleu et al. (2016). Similar hyperalkaline conditions occur during oil shale ash deposition and diagenesis. The water–ash slurry, initially depleted in dissolved carbon and enriched in Ca due to the fast exothermic slaking of free CaO and subsequent dissolution of portlandite, starts rapid precipitation of calcite on contact with atmospheric CO_2 . It is therefore highly likely that the low $\delta^{13}\text{C}$ values of

carbon bound to authigenic carbonate in oil shale ash deposits are not of organic origin. Negative $\delta^{13}\text{C}$ values are caused by the kinetic fractionation effects on both the diffusion of $\text{CO}_{2(\text{g})}$ and the hydroxylation of $\text{CO}_{2(\text{aq})}$ in the highly alkaline, bicarbonate-depleted and relatively low-temperature conditions in oil shale deposits. Similar processes have been demonstrated during carbonation of municipal waste ash where carbonate sediments form in a fluid oversaturated with Ca^{2+} ions. Negative $\delta^{13}\text{C}$ values are obtained, compared to systems in equilibrium, where the higher the activity of the ions, the more negative the $\delta^{13}\text{C}$ values of calcite become (Fléhoc et al. 2006). Such conditions are achieved by fluid in contact with portlandite or cement phases like C-S-H gel that can raise the pH of the fluid to over 12.5 (Létolle et al. 1992). The same kinetic fractionation process has also been observed in carbonate crusts and stalactites formed on old concrete structures as a result of chemical weathering of Ca-rich phases like C-S-H gel (Macleod et al. 1991; Krishnamurthy et al. 2003).

In the presence of portlandite the kinetic fractionation takes place upon the diffusion of CO_2 molecules, into the water film surrounding $\text{Ca}(\text{OH})_2$. The molecules containing lighter carbon (^{12}C) isotopes are preferred for carbonate formation and as a result the precipitating CaCO_3 is about -10‰ lower compared to gaseous CO_2 (Fléhoc et al. 2006). Adding this to the atmospheric CO_2 $\delta^{13}\text{C}$ value of around -8‰ , the resulting hypothetical $\delta^{13}\text{C}$ value of the Ca-carbonate precipitating under such conditions is -18‰ . This fits with the average measured $\delta^{13}\text{C}$ value of -17.2‰ in oil shale ash sediments in this study.

Large variation in the $\delta^{13}\text{C}$ values of carbonate in oil shale ash deposits, from equilibrium values, can be explained by the incorporation of residual carbonate (calcite) potentially present in bottom ash fraction. Alternatively, the variation can be explained by calcite precipitation at the later stages of carbonation when pH values are dropping below 9, approaching thus the equilibrium state. The more negative values hint at additional fractionation in different kinetic steps (Clark et al. 1992; Létolle et al. 1992). This results in a total maximum fractionation of $-15.5 \pm 1.5\text{‰}$ during hydroxylation of aqueous CO_2 , and final carbonate $\delta^{13}\text{C}$ value of -23‰ . This agrees with the minimum measured values of -21‰ to -22.95‰ in oil shale ash deposits and particularly in the laboratory experiment where the $\delta^{13}\text{C}$ values were even slightly more negative than in the oil shale ash plateau.

The variation in ambient temperature can influence the diffusion during kinetic fractionation adding to the extent of the fractionation on gaseous CO_2 . This view is supported by a weak covariation between measured carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Fig. 2). In general, the lowest $\delta^{13}\text{C}$ carbon isotope values also display the most

^{18}O depleted isotope composition. This would imply that higher temperatures during carbonation (as referred from oxygen isotopic composition), in fact, lead to more depleted ^{13}C isotope composition in carbonates. However, such direct comparison from oxygen isotopic composition to environmental temperatures cannot be made in this system far from the equilibrium state. This is further exemplified by the large variation in calculated temperatures for the ash deposit sediments ranging from 5.7 to 38.6 °C with an average value of 16.5 °C, and particularly by the temperatures for experimental samples 22.8 and 33.8 °C after two weeks and three months of curing, respectively (Fig. 3; Table 1). The laboratory experiment was performed at room temperature varying between 20 and 22 °C for the whole experiment period. After two weeks of curing, the calculated temperature using oxygen isotope fractionation thermometry agrees with the ambient temperature in the laboratory. However, after three months the calculated temperature significantly deviates from the ambient conditions in the laboratory.

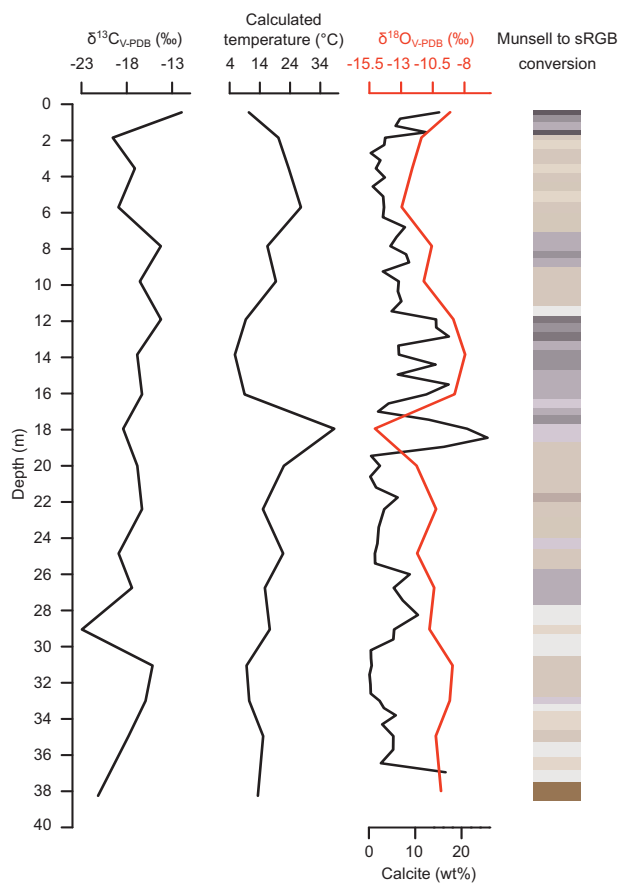


Fig. 3. Calculated equilibrium temperatures and Munsell colouration of samples compared to isotopic composition.

First of all, this depletion in the oxygen isotopic composition of authigenic calcite can be mainly attributed to reaction of $\text{CO}_{2(\text{aq})}$ with strongly ^{18}O -depleted OH^- (Clark et al. 1992) but it also signals strong kinetic effects on the oxygen isotopic composition of the authigenic carbonate precipitating in oil shale ash deposits. Furthermore, earlier studies of carbonates formed under DIC-depleted hyperalkaline conditions (Leleu et al. 2016; Teboul et al. 2016) show a similar positive trend between negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values that reflects the non-equilibrium isotopic shifts in dissolved inorganic carbon. This is due to progressive calcite precipitation (and CO_2 degassing in some environments) and makes the calculated temperatures, based on temperature-controlled equilibrium fractionation on the formation of carbonates, unreliable (Mickler et al. 2006). It is possible that during the deposition of large amounts of ash sediment, fast carbonation will locally deplete the solution reservoir of CO_3^{2-} carrying light oxygen whereas the diffusion and hydration, and hydroxylation reactions of CO_2 will not be fast enough to ensure isotopic equilibrium.

As discussed above, the highly negative $\delta^{13}\text{C}$ values of carbonates (-11.95‰ to -22.95‰) in ash sediment samples, typically associated with an organic origin of carbon, are likely of inorganic origin and result from kinetic fractionation effects in this unusually alkaline environment. This can further be tested by the possible covariation of organic-rich retorting ash beds and the isotopic composition of authigenic carbonate. Darker-coloured SHC oil retorting ash has a residual organic content of up to 3% (Talviste et al. 2013). Part of the carbon bound in carbonates may originate from the aerobic decomposition of this organic material or original oil shale, leading to the more negative $\delta^{13}\text{C}$ composition of the carbonate. However, no correlation between darker layers and the most negative $\delta^{13}\text{C}$ values could be made. Furthermore, the highest $\delta^{13}\text{C}$ value (-11.9‰ , depth 0.45 m) was found in a dark sample and the lowest value (-22.9‰ , depth 29.05 m) was measured in a white ash sample. The isotopic value of the stratigraphically highest samples can be skewed by the contribution from residual carbonate from CFBC ash. However, in deeper parts of the deposit, high-temperature PC ashes dominate without or with minimum residual carbonate content.

CONCLUSIONS

The isotopic composition of Ca-rich oil shale ash in ash waste deposits next to the power plants and shale oil retorts in Estonia was studied. The stable isotope composition of authigenic carbonate is characterized by $\delta^{13}\text{C}_{\text{V-PDB}}$ values between -12‰ and -24‰ and $\delta^{18}\text{O}_{\text{V-PDB}}$ between -8‰ and -15‰ . The negative isotopic composition of carbonate

carbon is typically interpreted to reflect the contribution of CO_2 derived from the degradation of residual organic material. However, the non-equilibrium fractionation effects in hyperalkaline conditions and limited CO_2 diffusion into the sediments cause the low $\delta^{13}\text{C}$ carbon isotope values of the oil shale ash deposits because the molecules of CO_2 containing lighter ^{12}C isotopes are preferred on diffusion into the water film surrounding $\text{Ca}(\text{OH})_2$ during carbonation. Non-equilibrium effects, likely due to local depletion of lighter isotopic CO_3^{2-} during carbonation, are also responsible for low oxygen isotopic values and the stable oxygen isotopic composition cannot reliably be used to estimate the equilibrium temperature of the solution during carbonate formation in oil shale ash deposit sediments.

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Supplementary online data

The supplementary online data table can be found at <https://doi.org/10.15152/GEO.491>. It contains Munsell colour system codes and the estimated relative oil retort ash content of the studied ash sediment samples.

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Kaltsiumirikka põlevkivituha sette stabiilsete süsiniku ja hapniku isotoopide geokeemiline uuring

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Eesti energeetikasektor sõltub kohalikust karbonaatsest põlevkivist toodetavast elektrienergiast. Põlevkivi põletamisel ja õli utmisel tekkivad tahked jäätmed ladestatakse valdavalt hüdrauliliselt tuhaväljadele ning need on potentsiaalselt võimelised õhust süsihappegaasi karbonaatsete mineraalide koostises tagasi siduma. Artiklis on uuritud ligi 50 aasta jooksul leeliselise tuhaväljale ladustatud kaltsiumirikka tuhasette autigeensete karbonaatsete faaside isotoopkoostist, selgitamaks karbonaadistumise mehhanismi ja seotava süsihappegaasi päritolu. Tuhasettes moodustunud sekundaarseid karbonaatseid faase iseloomustab tugevalt negatiivne $\delta^{13}\text{C}$ ja $\delta^{18}\text{O}$ suhtes vaesustunud stabiilsete isotoopide koostis $\delta^{13}\text{C}_{\text{V-PDB}}$ väärtustega vahemikus -12 kuni -24‰ ning $\delta^{18}\text{O}_{\text{V-PDB}}$ väärtustega vahemikus -8 kuni -15‰ . Näiliselt viitab negatiivne isotoopkoostis õlitootmise tuhas sisalduvast jääkorgaanikast pärit süsiniku sidumisele karbonaatides. Suure tõenäosusega on vaesustunud isotoopkoostis põhjustatud aga kõrgelt leeliselise keskkonna ja piiratud süsihappegaasi difusiooni tulemusel toimuvate mittetasakaaluliste fraktsioneerumise protsesside poolt.