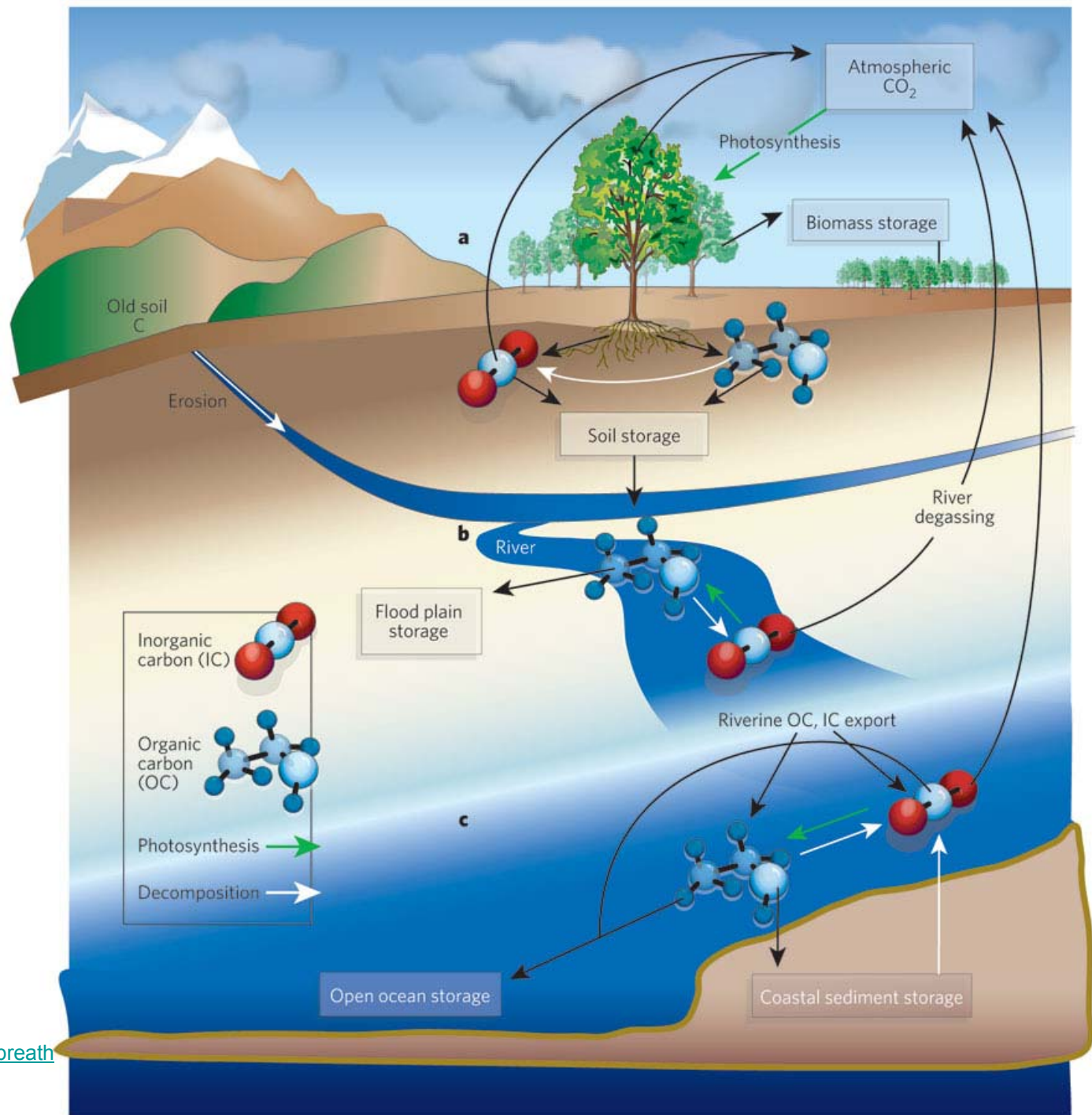


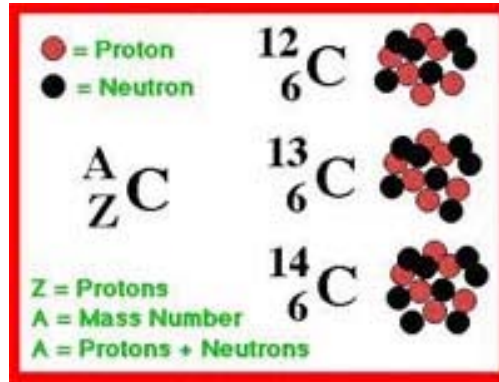
Ugljik



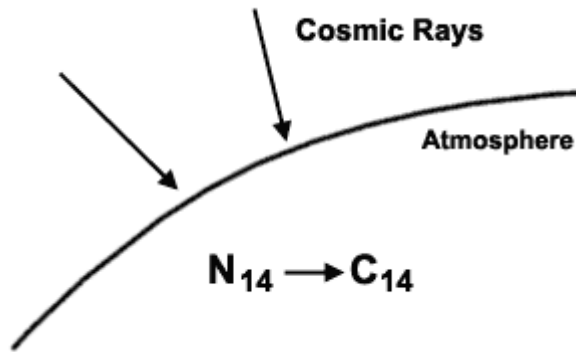
[Carbon cycle: The age of the Amazon's breath](#)
Peter A. Raymond
Nature 436, 469-470 (28 July 2005)

Izotopi ugljika

$^{12}\text{C}=98,89\%$
 $^{13}\text{C}=1,11\%$ } stabilni



^{14}C ($T_{1/2}=5715$ god) radioaktivan



Valentna stanja ugljika

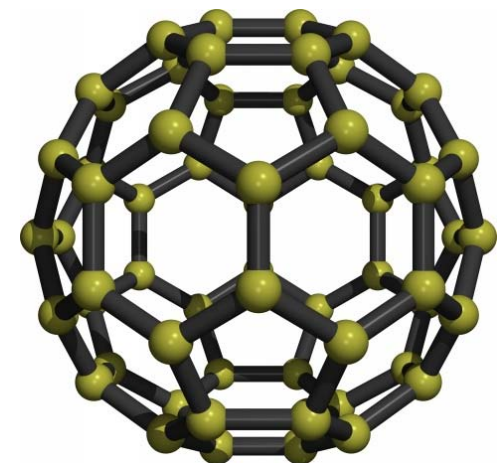
C^{4+}O_2
 C^{2+}O
 $\text{C}^0 \longrightarrow$ dijamant, grafit, fuleren
 C^{4-}H_4



dijamant



grafit



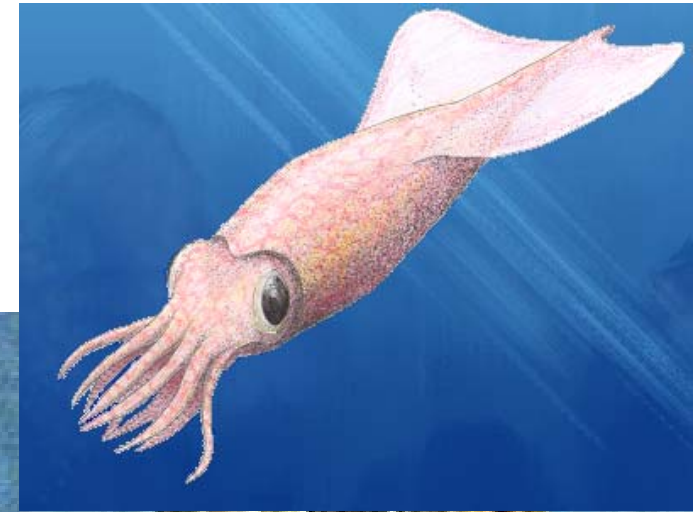
fuleren

δ-notacija

$$\delta^{13}\text{C} = \frac{(^{13}\text{O} / ^{12}\text{O})_{\text{samp}} - (^{13}\text{O} / ^{12}\text{O})_{\text{stand}}}{(^{13}\text{O} / ^{12}\text{O})_{\text{stand}}} \times 1000\%$$

Standard – CO₂ oslobođen tijekom reakcije belemnita iz Peedee formacije s 100%-tnom fosfatnom kiselinom

Belemnit iz Peedee formacije (*Belemnitella Americana*, Peedee formacija, Kreda, J. Karolina)



Belemnitella Americana

Ugljik u modernoj biosferi

Carbon Dioxide
and Water

$\delta^{13}\text{C}$ (atmosferski CO_2) = -7‰


Sunlight
Energy



Oxygen
Released

Carbohydrates
Formed

Kopnene biljke: -24 do -34 ‰
Vodene biljke, tropske trave: -6 do -19 ‰
Alge i lišajevi: -12 do -23 ‰



Životinje imaju $\delta^{13}\text{C}$ sličan
hrani koju jedu
(You are what you eat!)



Kopnene biljke: -24 do -34 ‰

Marinski karbonati: +2 ‰

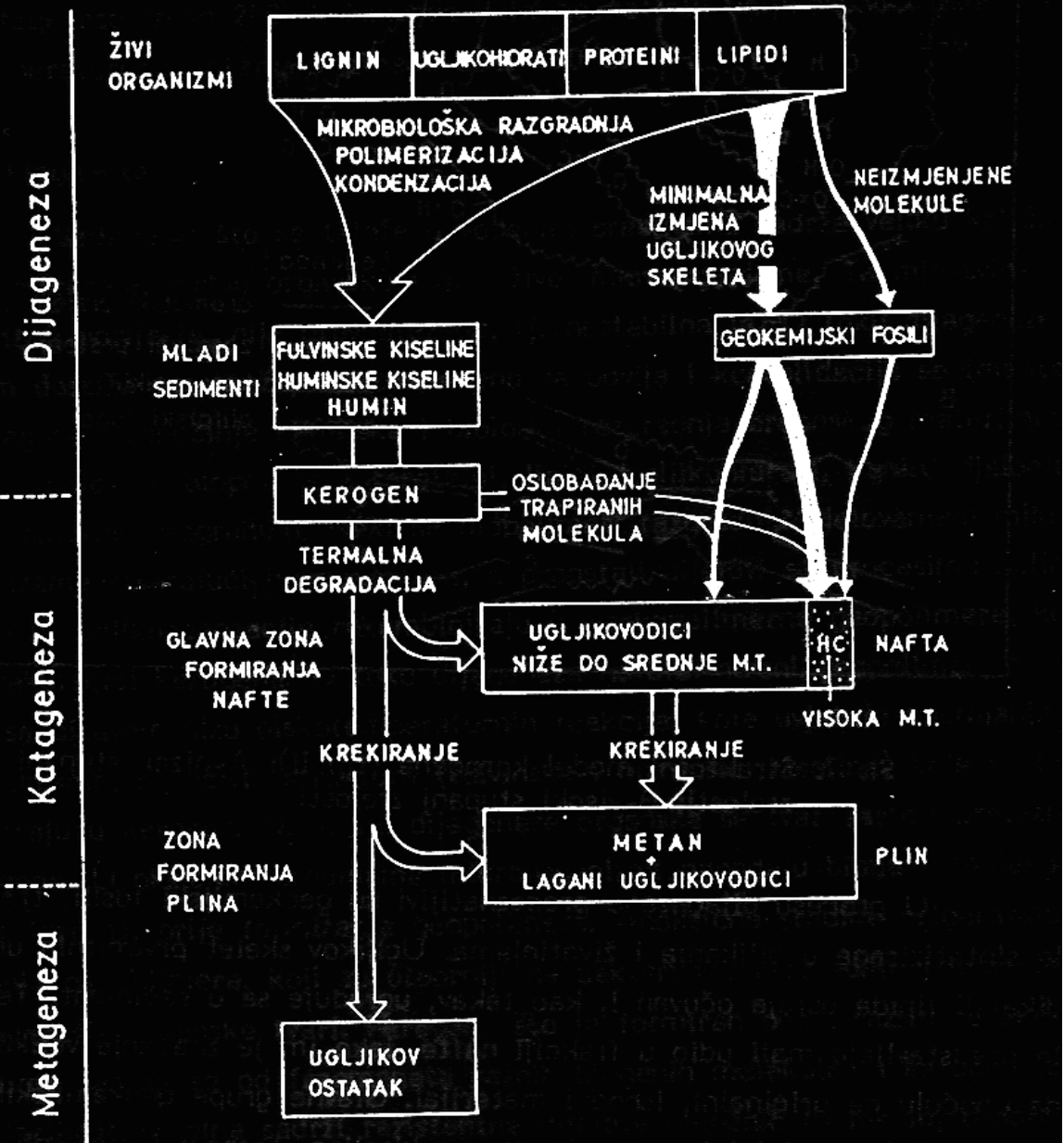
Karbonati u tlu: -11,5 ‰

Organska tvar u recentnim sedimentima: -10 do -30 ‰

Postoji li mogućnost određivanja porijekla organske tvari u sedimentima na bazi $\delta^{13}\text{C}$?
NE!!!

Dijageneza vodi prema obogaćenju na masti, lignin i celulozu

Organska tvar u recentnim sedimentima: -10 do -30 ‰ s maksimumom između -20 i -27 ‰



Fosilna goriva

Ugljen: -25‰ (ne mjenja se starenjem i karbonifikacijom ugljena)

Nafta: -28‰ (obogaćenje od ~10‰ na ^{12}C zbog načina postanka – uglavnom iz lipida s niskim vrijednostima $\delta^{13}\text{C}$)

Plin: -40 do -75‰ (CH_4 ima najniže vrijednosti $\delta^{13}\text{C}$, povećanje broja C-atoma u molekuli \rightarrow $\delta^{13}\text{C}$ raste)

Spaljivanje fosilnih goriva \rightarrow sniženje $\delta^{13}\text{C}$ u CO_2 u atmosferi

“Suess efekt” – sniženje ^{14}C jer fosilna goriva ne posjeduju ^{14}C

CO_2 u atmosferi 20-tog stoljeća raste s 290ppm (1900.) na 323ppm (1975.) te 380ppm (2000.)



Sedimentne stijene prekambrijske starosti

Tragovi organske tvari u prekambrijskim rožnjacima (3 milijarde god.!!!)

$\delta^{13}\text{C}$: -15 do -40 ‰ ukazuje na biološko porijeklo

- zbog gubitka metana omjer H/C pada



Stromatoliti iz North Pole ležišta u Zapadnoj Australiji (starost ~3.5 milijardi godina)

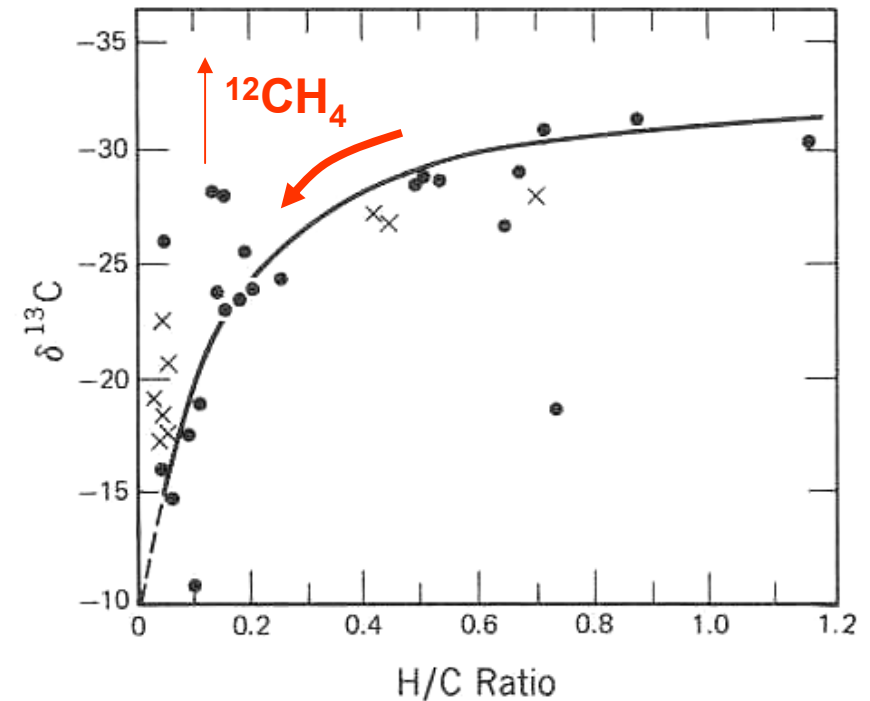
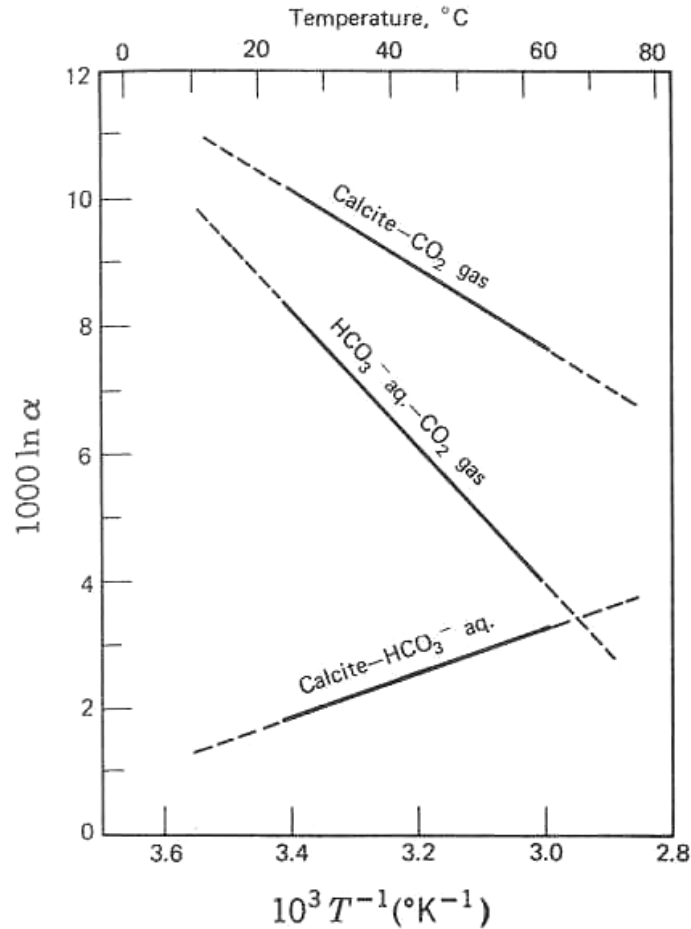
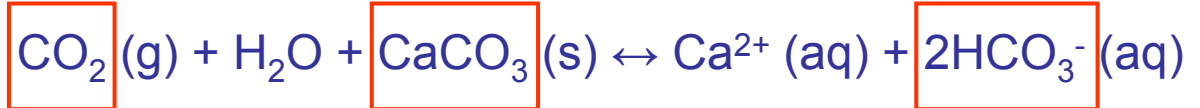


FIGURE 20.1 Plot of $\delta^{13}\text{C}$ of reduced carbon in sedimentary rocks of Precambrian to Middle Cambrian age versus the rank of the organic fraction as indicated by the atomic H/C ratio. The solid circles represent samples from Australia while the crosses are cherts from the Onverwacht Series of South Africa. These data suggest that organic carbon in sedimentary rocks is enriched in ^{13}C by the formation and subsequent loss of methane (which concentrates ^{12}C) during increasing thermal modification of kerogen as indicated by its atomic H/C ratio. (The data are from McKirdy and Powell, 1974.) The standard is PDB.

Marinski i nemarinski karbonati



Karbonatna ravnoteža:



$$\alpha_{AB} = \frac{\delta_A + 1000}{\delta_B + 1000}$$

FIGURE 20.2 Variation of carbon isotope fractionation in the system: CO₂ (gas) – HCO₃⁻ (aqueous) – CaCO₃ (solid) as a function of temperature. Note that 1000 ln α ≈ (α – 1) 1000 ≈ ΔAB, where A and B are two carbon-bearing phases in isotopic equilibrium and Δ is the difference between their δ values. If Δ = 8.8‰, the fractionation factor α = 1.0088. (Replotted from experimental data of Emrich et al., 1970.)

	α (20°C)
CaCO ₃ /HCO ₃	1,001185
HCO ₃ /CO ₂	1,00838
CaCO ₃ /CO ₂	1,01017

Primjer: CaCO_3 se taloži na 20°C , u ravnoteži s CO_2 ($\delta^{13}\text{C} = -7\text{‰}$). Izračunaj $\delta^{13}\text{C}(\text{CaCO}_3)$ na osnovu raspoloživih faktora frakcionacije.

Table 20.1 Variation of Carbon Isotope Fractionation Factors of Various Carbonate Species Relative to CO_2 Gas (Deines et al., 1974)

CARBONATE SPECIES	<i>A</i>	<i>B</i>
H_2CO_3 aq	0.0063	-0.91
HCO_3^- aq	1.099	-4.54
CO_3^{2-} aq	~0.87	~-3.4
CaCO_3 solid	1.194	-3.63

The equations are of the form:

$$1000 \ln \alpha = A(10^6 T^{-2}) + B$$



Marinski karbonati od kambrija do tercijara imaju prosječnu vrijednost $+0,56 \pm 1,55 \text{ ‰}$

Nemarinski (slatkovodni) karbonati obogaćeni su na ^{12}C te im vrijednosti jače variraju ($-4,43 \pm 2,75 \text{ ‰}$)

Dijagenetski procesi bitni su za konačni sastav vapnenaca

Rariteti:

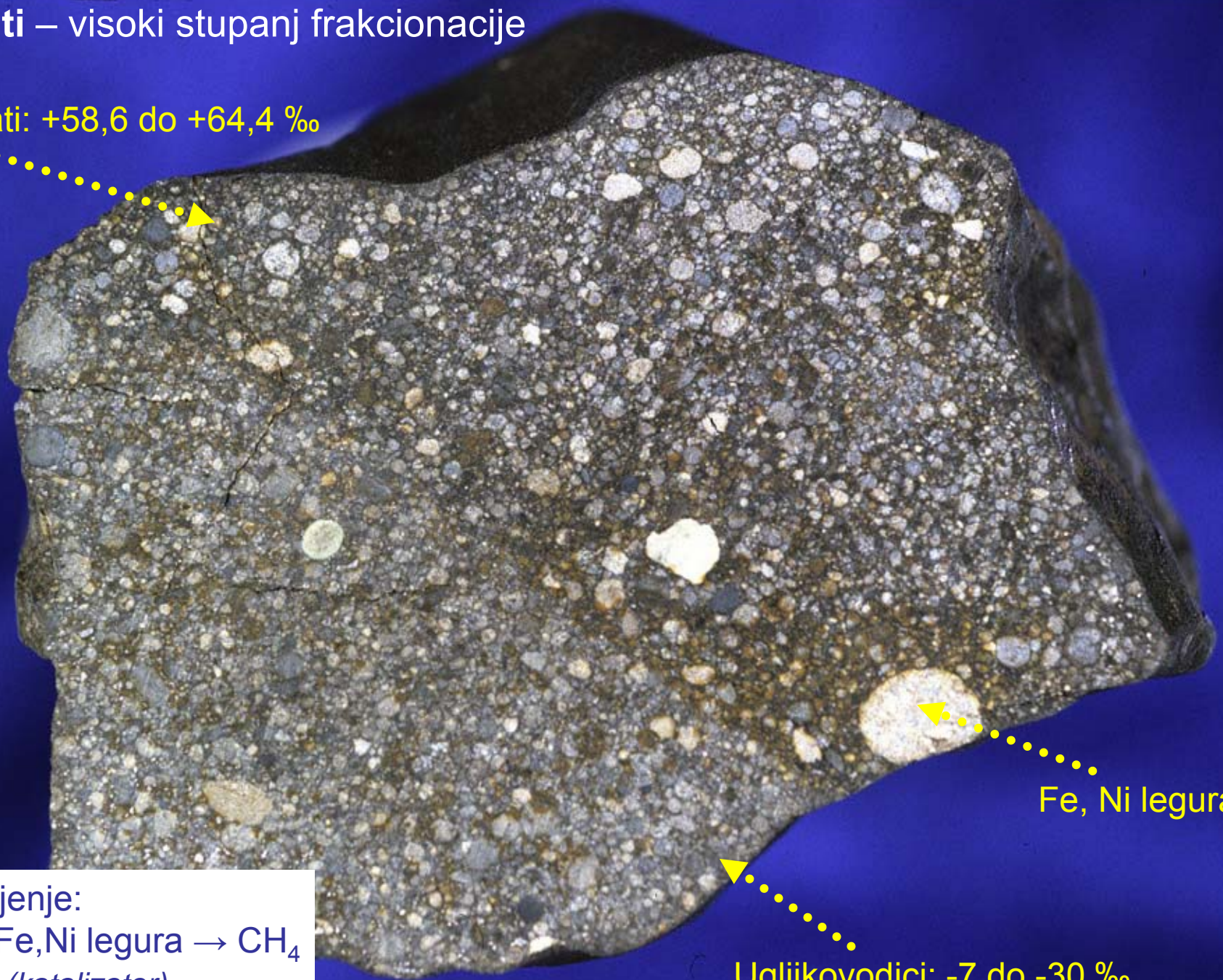
Aragonit u pleistocenskim pijescima na kont. šelfu (USA): $-23,1$ do $-60,6 \text{ ‰}$
Objašnjenje: CO_2 (HCO_3^-) je nastao oksidacijom metana

CaCO_3 iz pokrovnih stijena solnih doma u Gulf Coast(USA): $-36,2 \pm 6,2 \text{ ‰}$
Objašnjenje: CO_2 (HCO_3^-) je nastao bakterijskom oksidacijom metana

Kalcit asociran s organskim materijalom iz uranskih ležišta Windriver formacije (d. eocen): $-22,5 \pm 4,0 \text{ ‰}$
Objašnjenje: CO_2 (HCO_3^-) je nastao oksidacijom organskog detritusa

Hondriti – visoki stupanj frakcionacije

Karbonati: +58,6 do +64,4 ‰



Fe, Ni legura

Ugljikovodici: -7 do -30 ‰

Objašnjenje:



Karbonatiti i dijamanti

Subkristalno porijeklo iz alkalnih magmi bogatih karbonatom

$\delta^{13}\text{C}$: -2 do -8 ‰

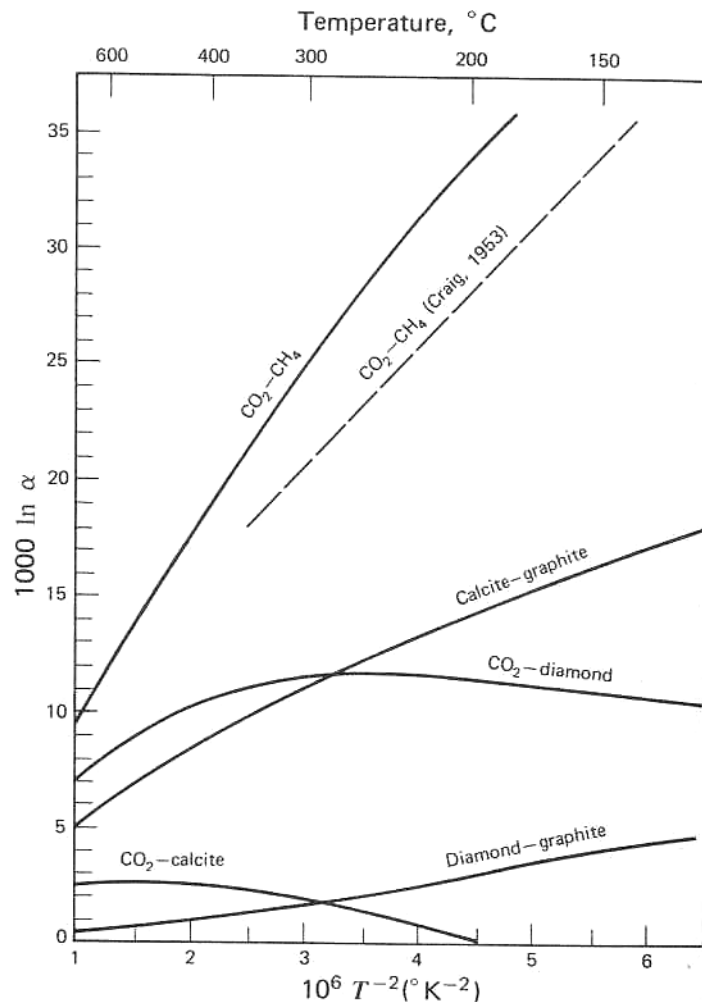


FIGURE 20.3 Calculated isotope fractionation factors for carbon in the system calcite- CO_2 -diamond-graphite- CH_4 . (Bottinga, 1969a, b; Craig, 1953.)

Dijamanti u kimberlitskim cijevima, geneza zahtjeva 1200°C , 45 kbara tj. ekvivalent 150km dubine

$\delta^{13}\text{C}$: -2 do -10 ‰

Frakcionacija je moguća sve do 1200°C

- Dijamanti ne predstavljaju izotopni sastav plašta jer reekvilibriraju s karbonatnim vrstama na putu prema površini Zemlje



Dijamant iz Jakutije (Sibir)

$\delta^{13}\text{C}$: -5 do -32,3 ‰

Vrijednosti se preklapaju s biološkim ugljikom

Pretpostavka: nastanak na nižoj temperaturi

Ugljik u magmatskim stijenama i vulkanskim plinovima

Reducirani ugljik: -20 do -28‰
 Oksidirani ugljik: +2,9 do -18‰

} Posljedica frakcionacije

Vulkanski plinovi: CO₂ (+1% CH₄)
 CH₄: -20 do -30‰ (znatno više od biogenog metana)

CO₂ + 4H₂ ↔ CH₄ + 2H₂O
 (vodene fumarole, Lorderello, Italija)

Frakcionacija

$\delta^{13}\text{C} (\text{CO}_2) = -3,74 \text{ ‰}$

$\delta^{13}\text{C} (\text{CH}_4) = -26,74 \text{ ‰}$

$\Delta(\text{CO}_2\text{-CH}_4) = 23 \text{ ‰}$

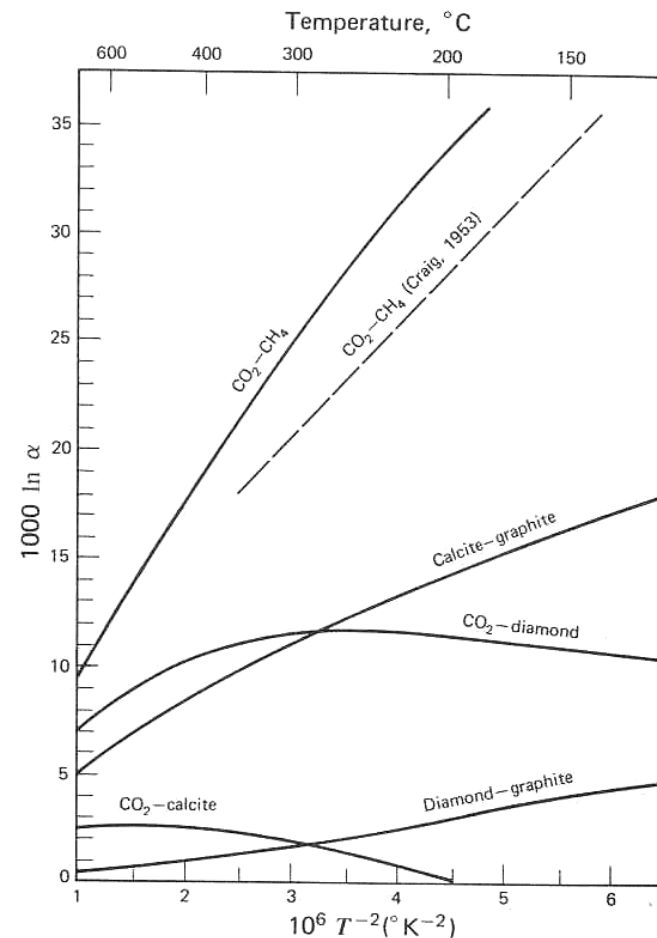
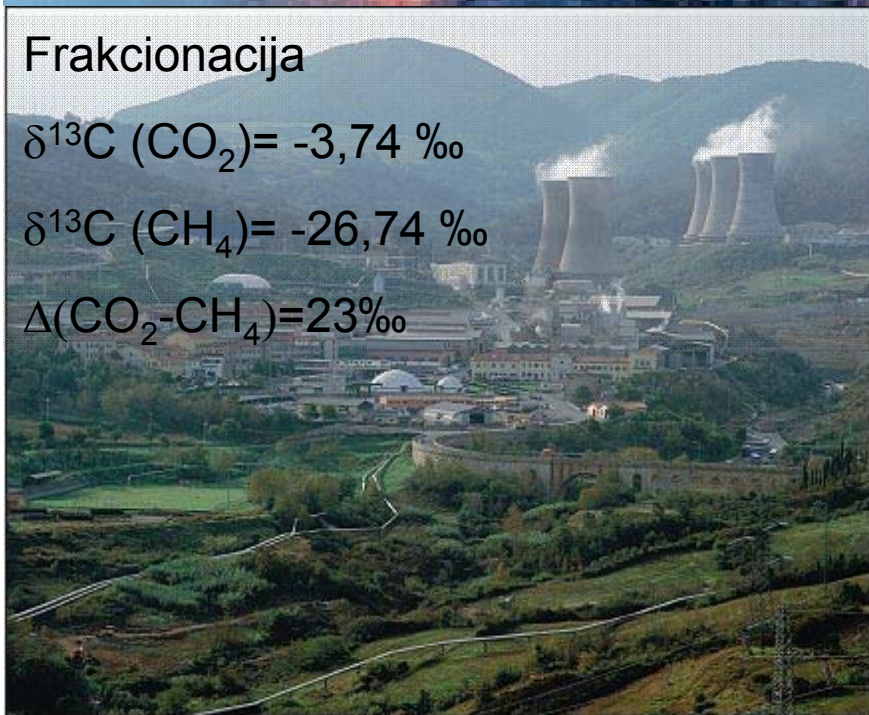


FIGURE 20.3 Calculated isotope fractionation factors for carbon in the system calcite-CO₂-diamond-graphite-CH₄. (Bottinga, 1969a, b; Craig, 1953.)

Mramori i grafit (I)

Mt. Royal, Montreal, Kanada
d. Kreda



Glinoviti vapnenac

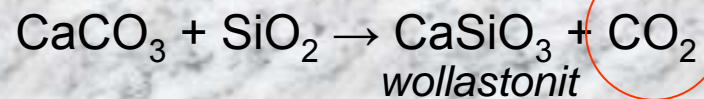
$\delta^{13}\text{C} = +1,13 \text{ ‰}$

$\delta^{18}\text{O} = +24,12 \text{ ‰}$

↑
Skarn
 $\delta^{13}\text{C} = -3,91 \text{ ‰}$
 $\delta^{18}\text{O} = +11,06 \text{ ‰}$

↑
Skarn
 $\delta^{13}\text{C} = -0,58 \text{ ‰}$
 $\delta^{18}\text{O} = +18,4 \text{ ‰}$

Pad $\delta^{13}\text{C}$ i $\delta^{18}\text{O}$ vrijednosti zbog dekarbonizacije i gubitka CO_2

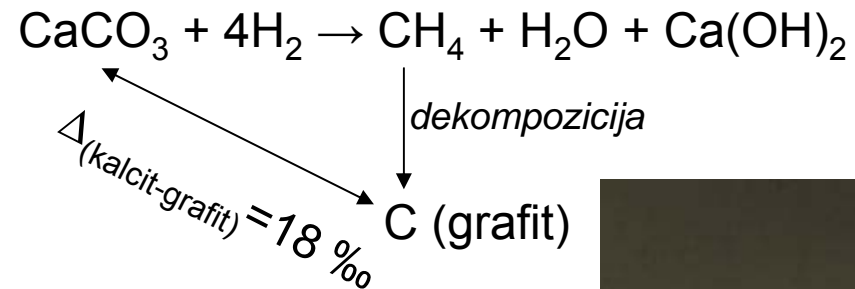


Obogaćen na ^{13}C i ^{18}O

Mramori i grafit (II)

Izotopna vrijednost ugljika u grafitu iz metamorfoziranih sedimenata približava se biogenom ugljiku

Grafit u meteoritima, ultrabazičnim stijenama i skarnovima je “težak” (-2 do -8 ‰, abiogeni)



Grafit u kalcitu

Hidrotermalna rudna ležišta

Ca, Mg, Fe, Mn-karbonati
 CO₂, CH₄ u inkluzijama

Izotopni sastav ovisi o fugacitetu
 kisika, pH, temperaturi, ionskoj
 jakosti i ukupnoj konc. ugljika

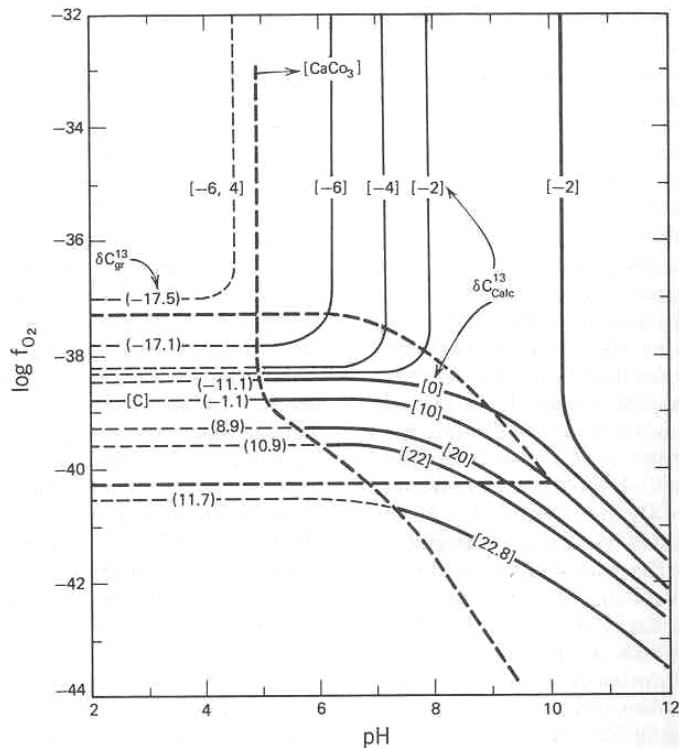
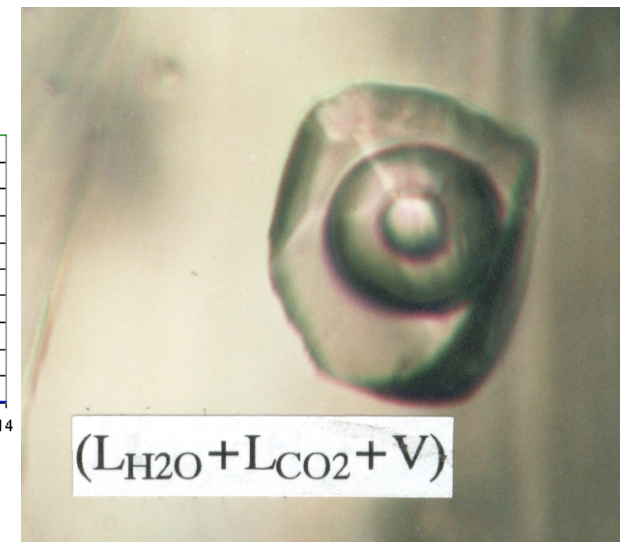
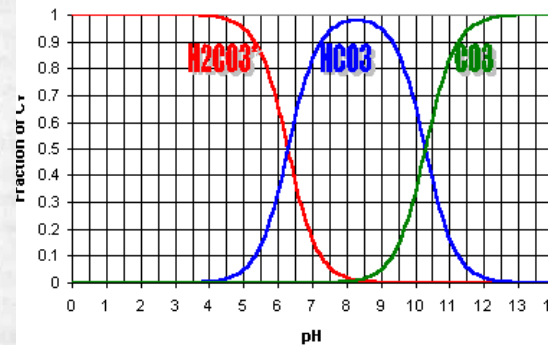


FIGURE 20.4 Possible variation of $\delta^{13}\text{C}$ values of calcite and graphite as functions of pH and the fugacity of oxygen. The diagram is based on the assumption that isotopic equilibrium is maintained and that the removal of solid phases does not affect the isotopic composition of the carbon remaining in solution. Temperature = 250°C, ionic strength = 1.0, $\delta^{13}\text{C}$ (total carbon) = -5 percent, total carbon concentration = 1 mole/kg H₂O. (Redrawn from H. Ohmoto, Economic Geology, 1972, vol. 67, No. 5, 551-578, Figure 14, with permission for the use of the diagram by H. Ohmoto.)



Kutnahorit, Trepča



Fl. inkluzija, kvarc, Sr. Bosna

Dušík

^{14}N
14.00307
99.63%
Stable

^{15}N
15.0001
0.37%
Stable

