$^{13}C/^{12}C$ of Industrial CO_2

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The average $\delta^{13}C$ (PDB) values of coal and lignite, petroleum and natural gas have been estimated from a number of data sources (see references). The adopted values for coal and lignite (−24.1‰) and petroleum (−26.5‰) are believed to be accurate to several tenths of a per mil, while the value for natural gas (−41.0‰) is uncertain by several per mil. For CO_2 from the production of cement, a value of 0.0‰ has been adopted, since the PDB standard itself is representative for limestones.

The principal problem in obtaining average values for the fossil fuels is that the interest in their $^{13}C/^{12}C$ ratios is focussed on how these relate to the origin and maturation of the various types of coal, petroleum and gaseous hydrocarbon deposits. Since we wish to know an average distribution of $\delta^{13}C$ in commercially mined deposits, our estimates may be biased because certain deposits have been studied very extensively, while others have hardly been examined at all.

The values for coal, from the different authors, coincide very well. Silverman (1967) has assembled thousands of measurements on petroleums and his estimate has been weighted accordingly. However, for the methane fraction of natural gas the values range from −20‰ to −75‰. The fractionation differs between wells and even changes with time for a given well. My best guess for an average is −43‰, which takes into account the fact that the methane of crude oil natural gas is usually 15−20‰ lighter isotopically than its associated oil, with a preferred average difference of 16‰. Natural gases typically also contain some ethane, propane and butane (carbon content ~16% of the total) that are less deficient in ^{13}C than methane. The fractionation of natural gas with respect to oil would then be about 14‰ and the preferred average for commercial natural gases would be −41‰.

The numbers in table 1 for the period from 1950 to the present have been computed from Rotty's data for global CO_2 production (this volume). For the period from 1850 to 1950 Keeling's (1973) tabulation has been used with a correction for flared gas (5.7% of petroleum, −41‰ $\delta^{13}C$) and with the cement production extrapolated backward.

Table 1. $\delta^{13}C$ of industrial CO_2

Year	$\delta^{13}C$	Year	$\delta^{13}C$	Year	$\delta^{13}C$	Year	$\delta^{13}C$
1850	−24.00	1890	−24.18	1920	−24.47	1950	−25.62
60	−24.00	91	−24.18	21	−24.49	51	−25.71
70	−24.00	92	−24.18	22	−24.52	52	−25.79
71	−24.00	93	−24.20	23	−24.59	53	−25.85
72	−24.00	94	−24.20	24	−24.62	54	−25.85
73	−24.01	95	−24.20	25	−24.66	55	−25.90
74	−24.02	96	−24.22	26	−24.71	56	−25.91
75	−24.01	97	−24.22	27	−24.74	57	−25.95
76	−24.02	98	−24.22	28	−24.79	58	−25.99
77	−24.02	99	−24.21	29	−24.81	59	−26.05
78	−24.02	1900	−24.22	1930	−24.84	1960	−26.13
79	−24.03	01	−24.24	31	−24.90	61	−26.32
1880	−24.05	02	−24.25	32	−24.92	62	−26.38
81	−24.06	03	−24.25	33	−24.90	63	−26.45
82	−24.09	04	−24.27	34	−24.93	64	−26.52
83	−24.06	05	−24.27	25	−24.93	65	−26.61
84	−24.08	06	−24.26	36	−24.95	66	−26.70
85	−24.10	07	−24.26	37	−24.99	67	−26.87
86	−24.12	08	−24.32	38	−25.00	68	−26.94
87	−24.13	09	−24.31	39	−25.00	69	−27.05
88	−24.15	1910	−24.31	1940	−24.98	1970	−27.17
89	−24.16	11	−24.32	41	−24.93	71	−27.28
		12	−24.32	42	−24.99	72	−27.26
		13	−24.32	43	−25.06	73	−27.29
		14	−24.37	44	−25.17	74	−27.28
		15	−24.39	45	−25.42	75	−27.21
		16	−24.41	46	−25.42	76	−27.26
		17	−24.42	47	−25.41	77	−27.29
		18	−24.40	48	−25.50	78	−27.28
		19	−24.46	49	−25.57		

REFERENCES

CO_2 data

Keeling, C.D. (1973). Industrial production of carbon dioxide from fossil fuels and limestone. Tellus *25,* 174−197.

Coals − isotopic data

Craig, H. (1953). The geochemistry of the stable carbon isotopes. Geochim. cosmochim Acta *3*, 53−92.

Compston, W. (1960). The carbon isotopic compositions of certain marine invertebrates and coals from the Australian Permian. Geochim. Cosmochim. Acta *18*, 1−22.

Garcia-Loygorri, A., Bosch, B. and Marcé, A. (1974). Etude isotopique du carbone de différentes couches du basin houiller central des Asturies (Espagne). In: Tissot, B. and Bienner, F. (eds). Adv. Org. Geochem., proc. 6th intern. meet, 859−873. Edit. Tech., Paris.

Jeffery, P.M., Compston, W., Greenhalgh, D. and de Laeter, I. (1955). On the carbon-13 abundance of limestones and coals. Geochim. Cosmochim. Acta *7*, 255–286.
Wickman, F.E. (1953). Wird das Häufigkeitsverhältnis der Kohlenstoffisotopen bei der Inkohlung verändert? Geochim. Cosmochim. Acta *3*, 244–252.

Petroleums – isotopic data

Eckelmann, W.R., Broecker, W.S., Whitlock, D.W. and Allsup, J.R. (1962). Implications of carbon isotopic composition of total organic carbon of some recent sediments and ancient oils. Bull. Amer. Assoc. Petroleum Geologists, *46*, 699–703.
Nagy, B. (1966). A study of the optical rotation of lipids extracted from soils, sediments and the Orgueil carbonaceous meteorite. Proc. Nat. Acad. Sci. *56*, 389–398.
Silverman, S.R. (1967). Carbon isotopic evidence for the role of lipids in petroleum formation. Journal Amer. Oil Chemists' Society *44*,, 691–695.

Natural gases – isotopic data

Colombo, U., Gazzarini, F., Gonfiantini, R., Kneuper, G., Teichmüller, M. and Teichmüller, R. (1966). Carbon isotope study on methane from German coal deposits. In: Adv. Org. Geochem., proc. 3rd int. meeting. (ed. G.D. Hobson and G.C. Speers), 1–26. Pergamon. London.
Sackett, W.M. and Menendez, R. (1972). Carbon isotopic study of the hydrocarbons and kerogen in the Aquitaine Basin, Southwest France. In: Adv. Org. Geochem., proc. 5th int. meet. (ed. H.R.V. Gaertner and H. Wehner), 523–533. Pergamon, Oxford.
Sackett, W.N., Nakaparksin, S. and Dalrymple, D. (1966). Carbon isotope effects in methane production by thermal cracking. In: Hobson, G.D. and Speers, G.C. (eds) Adv. Org. Geochem., proc 3rd int. meet., 37–53. Pergamon, London.
Stahl, W. (1974). Carbon isotope ratios of German natural gases in comparison with isotope data of gaseous hydrocarbons from other parts of the world. In: Tissot, B. and Bienner, F. (eds) Adv. Org. Geochem., proc. 6th int. meet., 453–462. Edit. Tech., Paris.
Wasserburg, G.J., Mazor, E. and Zartman, R.E. (1963). Isotopic and chemical composition of some terrestrial natural gases. In: Geiss, J. and Goldberg, e.D. (eds). Earth Science and Meteorites, 219–239. North-Holland Publ., Amsterdam.
Zartman, R.E., Wasserburg, G.J. and Reynolds, J.H. (1961) Helium, argon and carbon in some natural gases. J. Geophys. Res. *66*, 277–303.