Supplemental Information
Abiotic and biotic processes that drive carboxylation and decarboxylation reactions

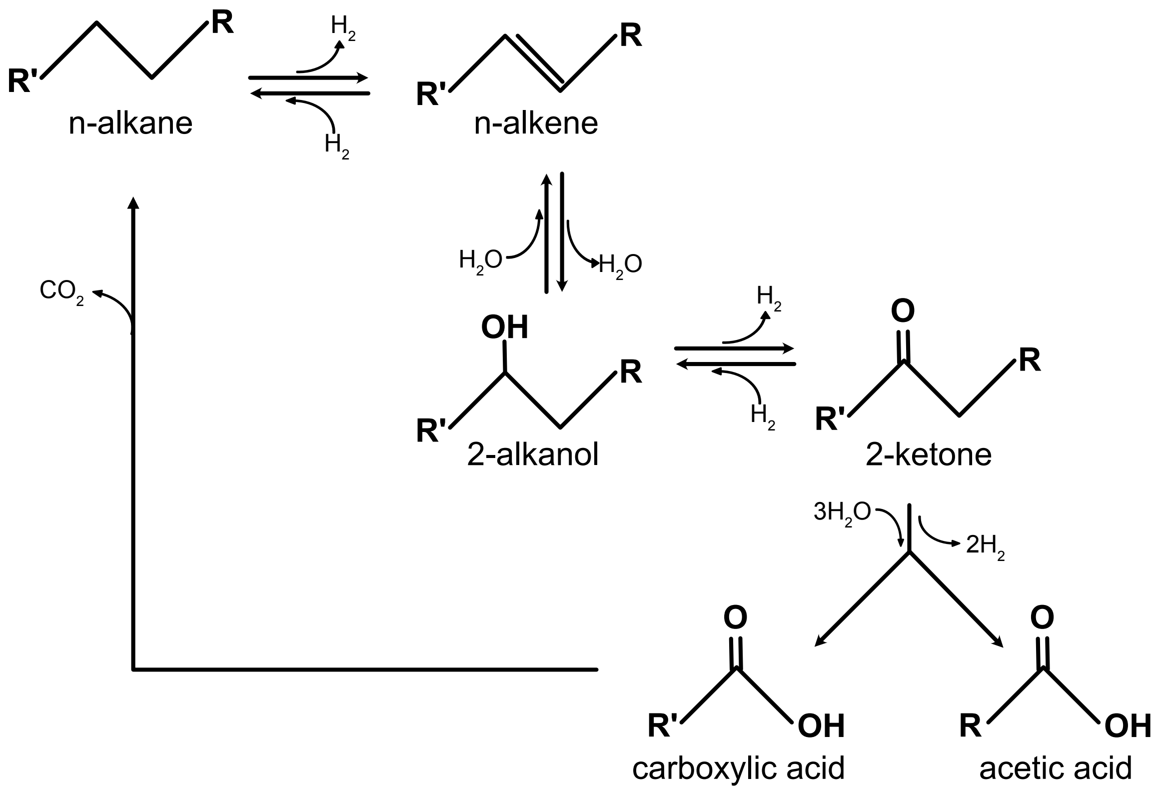
Cody S. Sheik[1*], H. James Cleaves II[2,3,4], Kristin Johnson-Finn[5], Donato Giovannelli[5,6,7,8], Thomas L. Kieft[9], Dominic Papineau[10,11,12], Matthew O. Schrenk[13], Simone Tumiati[14]

[1]Department of Biology and the Large Lakes Observatory, University of Minnesota Duluth, Duluth, MN, USA
[2]Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-1 Ookayama Meguro-ku, Tokyo 152-8550, Japan
[3]Institute for Advanced Study, 1 Einstein Drive, Princeton, NJ 08540, USA
[4]Blue Marble Space Institute of Science, Seattle, 98154, WA, USA
[5]Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-1 Ookayama Meguro-ku, Tokyo 152-8550, Japan
[6]Department of Biology, University of Naples "Federico II", Monte Sant'Angelo, 80120 Naples, Italy
[7]Department of Marine and Coastal Science, Rutgers University, 71 Dudley Road, 08901, New Brunswick, NJ, USA
[8] Institute for Marine Biological and Biotechnological Resources, National Research Council of Italy, CNR-IRBIM, Ancona, Italy
[9]New Mexico Institute of Mining and Technology, Socorro, NM, 87801, USA
[10]London Centre for Nanotechnology, 17-19 Gordon Street, University College London, London WC1H 0AH, UK
[11]Department of Earth Sciences, University College London, London WC1E 6BT, UK
[12]Centre for Planetary Sciences, University College London and Birkbeck University of London, London WC1E 6BT, UK
[13]Department of Earth and Environmental Sciences, Michigan State University, East Lansing, MI, USA, schrenkm@msu.edu
[14]Dipartimento di Scienze della Terra, University of Milan, via Mangiagalli 34, 20133 Milan, Italy, simone.tumiati@unimi.it

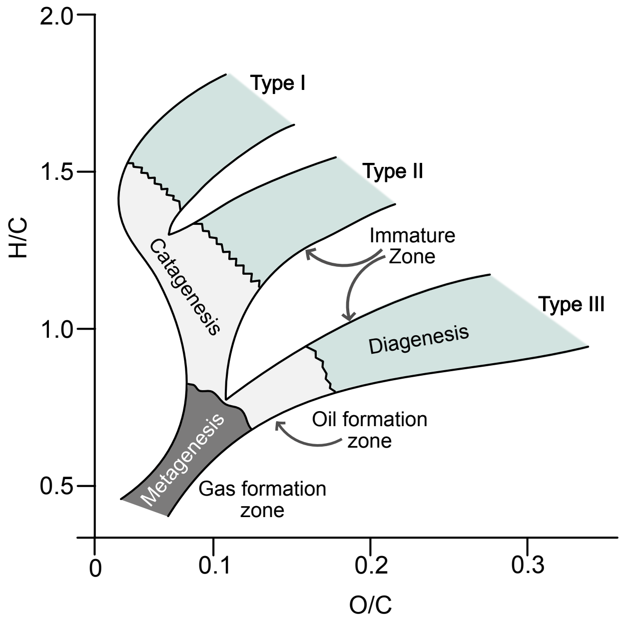
*Corresponding author Cody S. Sheik, cssheik@d.umn.edu, Department of Biology and the Large Lakes Observatory, University of Minnesota Duluth, Duluth, MN, USA

Supplemental Table 1. C-O-H organic compounds investigated in high pressure-high temperature experiments.

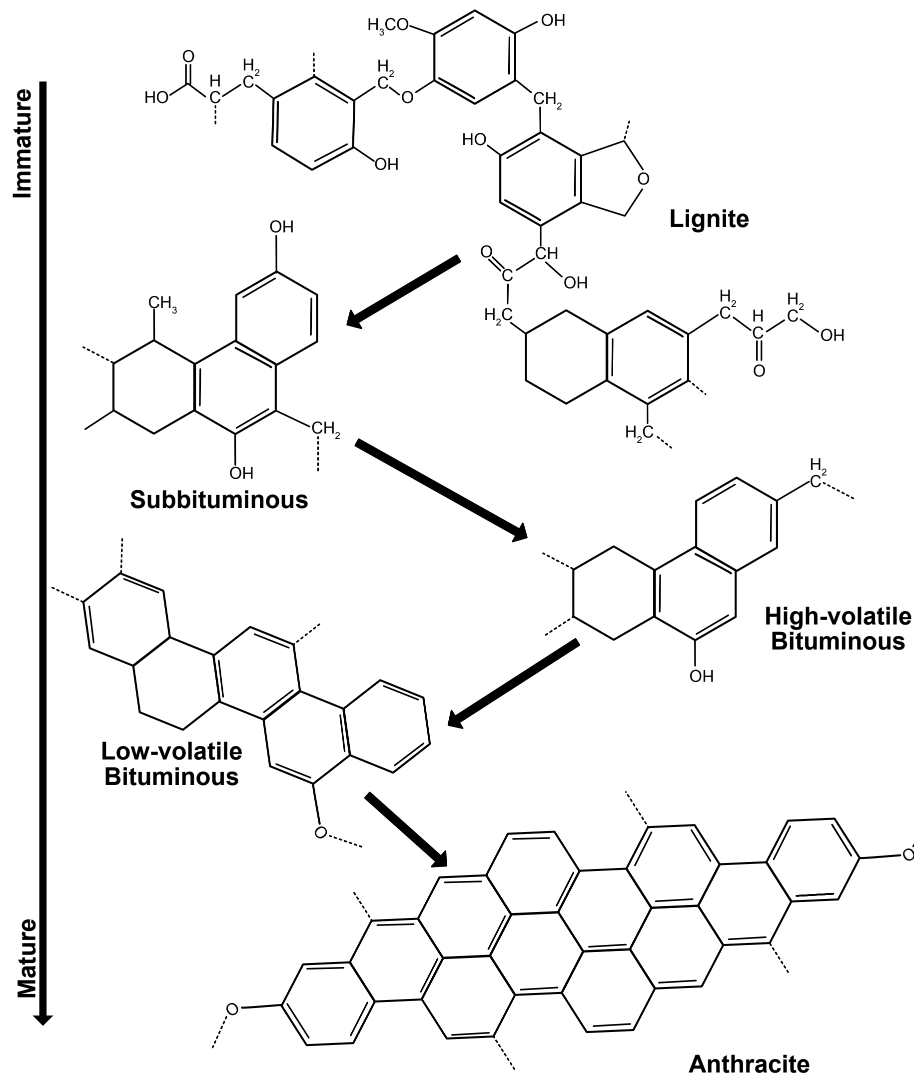
Compound	Molecular Formula	References
oxalic acid dihydrate	$C_2H_6O_6$	(Holloway et al. 1968; L. Millhollen et al. 1971; Holloway and Reese 1974; Kesson and Holloway 1974; Taylor and Liou 1978; Morgan et al. 1992; Rosenbaum and Slagel 1995; Draper and Green 1997; Aranovich and Newton 1999; Akaishi et al. 2000; Litvinovsky et al. 2000; Molina and Poli 2000; Newton and Manning 2000, 2009; Shmulovich et al. 2001, 2006; Sokol et al. 2001; Dobrzhinetskaya et al. 2004; Cherniak and Watson 2007, 2010; Poli et al. 2009, 2009; Tumiati et al. 2012, 2017; McCubbin et al. 2014; Poli 2015; Tiraboschi et al. 2016, 2017)
oxalic acid anhydrous	$C_2H_2O_4$	(Shaji Kumar et al. 2000; Tiraboschi et al. 2017; Tumiati et al. 2017)
stearic acid	$C_{18}H_{36}O_2$	(Taylor and Foley 1989; Matveev et al. 1997; Akaishi et al. 2000; Jakobsson and Holloway 2008; Sokol et al. 2009)
fumaric acid	$C_4H_4O_4$	(Eggler et al. 1979; Truckenbrodt et al. 1997; Truckenbrodt and Johannes 1998)
phthalic acid	$C_8H_6O_4$	(Matveev et al. 1997)
benzoic acid	$C_7H_6O_2$	(Matveev et al. 1997)
4'-acetophenone	$C_9H_{10}O_2$	(Truckenbrodt et al. 1997)
4'-Methoxy-acetophenone	$C_9H_{10}O_2$	(Truckenbrodt and Johannes 1998)
4-(1,1,3,3-Tetramethyl-butyl)-phenol	$C_{14}H_{22}O$	(Truckenbrodt et al. 1997)
3-(2-Furyl)-acrylic-acid	$C_7H_6O_3$	(Truckenbrodt and Johannes 1998)
formic acid	CH_2O_2	(Li 2017)
glucose	$C_6H_{12}O_6$	(Yamaoka et al. 2002)
acetic acid	$C_2H_4O_2$	(Huang et al. 2017)
anthracene	$C_{14}H_{10}$	(Matveev et al. 1997; Sokol et al. 2001, 2009)
n-hexacosane	$C_{26}H_{54}$	(Taylor and Foley 1989)
docosane	$C_{22}H_{46}$	(Sokol et al. 2009)



SI Figure 1. Retooling of the Seewald (2003) alkane decarboxylation reactions, whereby a long-chain alkane is shortened with stepwise decarboxylation reactions.



SI Figure 2. Van Krevelen diagram for the chemical evolution of sedimentary organic from diagenesis, through catagenesis and to metagenesis (based on (Seewald 2003; Vandenbroucke and Largeau 2007). Note that the main zone of oil formation is during catagenesis, which involves abiotic thermocatalytic decarboxylation.



SI Figure 3. A schematic of the process of coal maturation, which progressively depletes the original biological organic material in heteroatoms and hydrogen.

References

Akaishi, M., Shaji Kumar, M.D., Kanda, H., and Yamaoka, S. (2000) Formation process of diamond from supercritical H2O–CO2 fluid under high pressure and high temperature conditions. Diamond and Related Materials, 9, 1945–1950.

Aranovich, L.Y., and Newton, R.C. (1999) Experimental determination of CO2-H2O activity-composition relations at 600–1000 °C and 6–14 kbar by reversed decarbonation and dehydration reactions. American Mineralogist, 84, 1319–1999.

Cherniak, D.J., and Watson, E.B. (2007) Ti diffusion in zircon. Chemical Geology, 242, 470–483.

Cherniak, D.J., and Watson, E.B. (2010) Li diffusion in zircon. Contributions to Mineralogy and Petrology, 160, 383–390.

Dobrzhinetskaya, L.F., Renfro, A.P., and Green, H.W., II (2004) Synthesis of skeletal diamonds: Implications for microdiamond formation in orogenic belts. Geology, 32, 869–872.

Draper, D.S., and Green, T.H. (1997) P–T Phase Relations of Silicic, Alkaline, Aluminous Mantle-Xenolith Glasses Under Anhydrous and C–O–H Fluid-saturated Conditions. Journal of Petrology, 38, 1187–1224.

Eggler, D.H., Kushiro, I., and Holloway, J.R. (1979) Free energies of decarbonation reactions at mantle pressures; I, Stability of the assemblage forsterite-enstatite-magnesite in the system MgO-SiO 2 -CO 2 -H 2 O to 60 kbar. American Mineralogist, 64, 288–293.

Holloway, J.R., and Reese, R.L. (1974) The Generation of N2-CO2-H2O Fluids for Use in Hydrothermal Experimentation I. Experimental Method and Equilibrium Calculations in the C-O-H-N System. American Mineralogist, 59, 587–597.

Holloway, J.R., Burnham, C.W., and Millhollen, G.L. (1968) Generation of H2O-CO2 Mixtures for Use in Hydrothermal Experimentation. Journal of Geophysical Research (1896-1977), 73, 6598–6600.

Huang, F., Daniel, I., Cardon, H., Montagnac, G., and Sverjensky, D.A. (2017) Immiscible hydrocarbon fluids in the deep carbon cycle. Nature Communications, 8, 15798.

Jakobsson, S., and Holloway, J.R. (2008) Mantle melting in equilibrium with an Iron–Wüstite–Graphite buffered COH-fluid. Contributions to Mineralogy and Petrology, 155, 247–256.

Kesson, S.E., and Holloway, J.R. (1974) The Generation of N2-CO2-H2O Fluids for Use in Hydrothermal Experimentation II. Melting of Albite in a Multispecies Fluid. American Mineralogist, 59, 598–603.

L. Millhollen, G., J. Wyllie, P., and Wayne Burnham, C. (1971) Melting relations of NaAlSi 3 O 8 to 30 Kb in the presence of H 2 O:CO 2 = 50:50 vapor, 473 p. Vol. 271.

Li, Y. (2017) Immiscible C-H-O fluids formed at subduction zone conditions. Geochemical Perspectives Letters, 3, 12–21.

Litvinovsky, B.A., Steele, I.M., and Wickham, S.M. (2000) Silicic Magma Formation in Overthickened Crust: Melting of Charnockite and Leucogranite at 15, 20 and 25 kbar. Journal of Petrology, 41, 717–737.

Matveev, S., Ballhaus, C., Fricke, K., Truckenbrodt, J., and Ziegenben, D. (1997) Volatiles in the Earth’s mantle: I. Synthesis of CHO fluids at 1273 K and 2.4 GPa. Geochimica et Cosmochimica Acta, 61, 3081–3088.

McCubbin, F.M., Sverjensky, D.A., Steele, A., and Bjorn O. (2014) In-situ characterization of oxalic acid breakdown at elevated P and T: Implications for organic C-O-H fluid sources in petrologic experiments. American Mineralogist, 99, 2258.

Molina, J., and Poli, S. (2000) Carbonate stability and fluid composition in subducted oceanic crust: an experimental study on H 2O–CO 2-bearing basalts, 295 p. Vol. 176.

Morgan, G.B., Chou, I.-M., and Pasteris, J.D. (1992) Speciation in experimental C-O-H fluids produced by the thermal dissociation of oxalic acid dihydrate. Geochimica et Cosmochimica Acta, 56, 281–294.

Newton, R.C., and Manning, C.E. (2000) Quartz solubility in H2O-NaCl and H2O-CO2 solutions at deep crust-upper mantle pressures and temperatures: 2–15 kbar and 500–900°C. Geochimica et Cosmochimica Acta, 64, 2993–3005.

Newton, R.C., and Manning, C.E. (2009) Hydration state and activity of aqueous silica in H2O-CO2 fluids at high pressure and temperature. American Mineralogist, 94, 1287–1290.

Poli, S. (2015) Carbon mobilized at shallow depths in subduction zones by carbonatitic liquids Vol. 8.

Poli, S., Franzolin, E., Fumagalli, P., and Crottini, A. (2009) The transport of carbon and hydrogen in subducted oceanic crust: An experimental study to 5 GPa. Earth and Planetary Science Letters, 278, 350–360.

Rosenbaum, J.M., and Slagel, M.M. (1995) C-O-H speciation in piston-cylinder experiments. American Mineralogist, 80, 109–114.

Shaji Kumar, M.D., Akaishi, M., and Yamaoka, S. (2000) Formation of diamond from supercritical H2O–CO2 fluid at high pressure and high temperature. Journal of Crystal Growth, 213, 203–206.

Shmulovich, K., Graham, C., and Yardley, B. (2001) Quartz, albite and diopside solubilities in H2O–NaCl and H2O–CO2 fluids at 0.5–0.9 GPa. Contributions to Mineralogy and Petrology, 141, 95–108.

Shmulovich, K.I., Yardley, B.W.D., and Graham, C.M. (2006) Solubility of quartz in crustal fluids: experiments and general equations for salt solutions and H2O–CO2 mixtures at 400–800°C and 0.1–0.9 GPa. Geofluids, 6, 154–167.

Sokol, A.G., Pal'yanov, Yu.N., Pal'yanova, G.A., Khokhryakov, A.F., and Borzdov, Yu.M. (2001) Diamond and graphite crystallization from C–O–H fluids under high pressure and high temperature conditions. Diamond and Related Materials, 10, 2131–2136.

Sokol, A.G., Palyanova, G.A., Palyanov, Y.N., Tomilenko, A.A., and Melenevsky, V.N. (2009) Fluid regime and diamond formation in the reduced mantle: Experimental constraints. Geochimica et Cosmochimica Acta, 73, 5820–5834.

Taylor, B.E., and Liou, J.G. (1978) The low-temperature stability of andradite in C-O-H fluids. American Mineralogist, 63, 378–393.

Taylor, W.R., and Foley, S.F. (1989) Improved oxygen-buffering techniques for C-O-H fluid-saturated experiments at high pressure. Journal of Geophysical Research: Solid Earth, 94, 4146–4158.

Tiraboschi, C., Tumiati, S., Recchia, S., Miozzi, F., and Poli, S. (2016) Quantitative analysis of COH fluids synthesized at HP–HT conditions: an optimized methodology to measure volatiles in experimental capsules. Geofluids, 16, 841–855.

Tiraboschi, C., Tumiati, S., Sverjensky, D., Pettke, T., Ulmer, P., and Poli, S. (2017) Experimental determination of magnesia and silica solubilities in graphite-saturated and redox-buffered high-pressure COH fluids in equilibrium with forsterite + enstatite and magnesite + enstatite. Contributions to Mineralogy and Petrology, 173, 2.

Truckenbrodt, J., and Johannes, W. (1998) The effect of fO2 on phase relations and melt composition in a partially molten amphibolite, 409 p. Vol. 172.

Truckenbrodt, J., Ziegenbein, D., and Johannes, W. (1997) Redox conditions in piston-cylinder apparatus; the different behavior of boron nitride and unfired pyrophyllite assemblies. American Mineralogist, 82, 337–344.

Tumiati, S., Fumagalli, P., Tiraboschi, C., and Poli, S. (2012) An Experimental Study on COH-bearing Peridotite up to 3·2 GPa and Implications for Crust–Mantle Recycling. Journal of Petrology, 54, 453–479.

Tumiati, S., Tiraboschi, C., Sverjensky, D.A., Pettke, T., Recchia, S., Ulmer, P., Miozzi, F., and Poli, S. (2017) Silicate dissolution boosts the CO2 concentrations in subduction fluids. Nature Communications, 8, 616.

Yamaoka, S., Shaji Kumar, M.D., Kanda, H., and Akaishi, M. (2002) Thermal decomposition of glucose and diamond formation under diamond-stable high pressure–high temperature conditions. Diamond and Related Materials, 11, 118–124.