Il ciclo profondo del carbonio: rilascio e trasporto di CO_2 dal mantello all'esosfera

Maria Luce Frezzotti

Dipartimento di Scienze della Terra, Siena

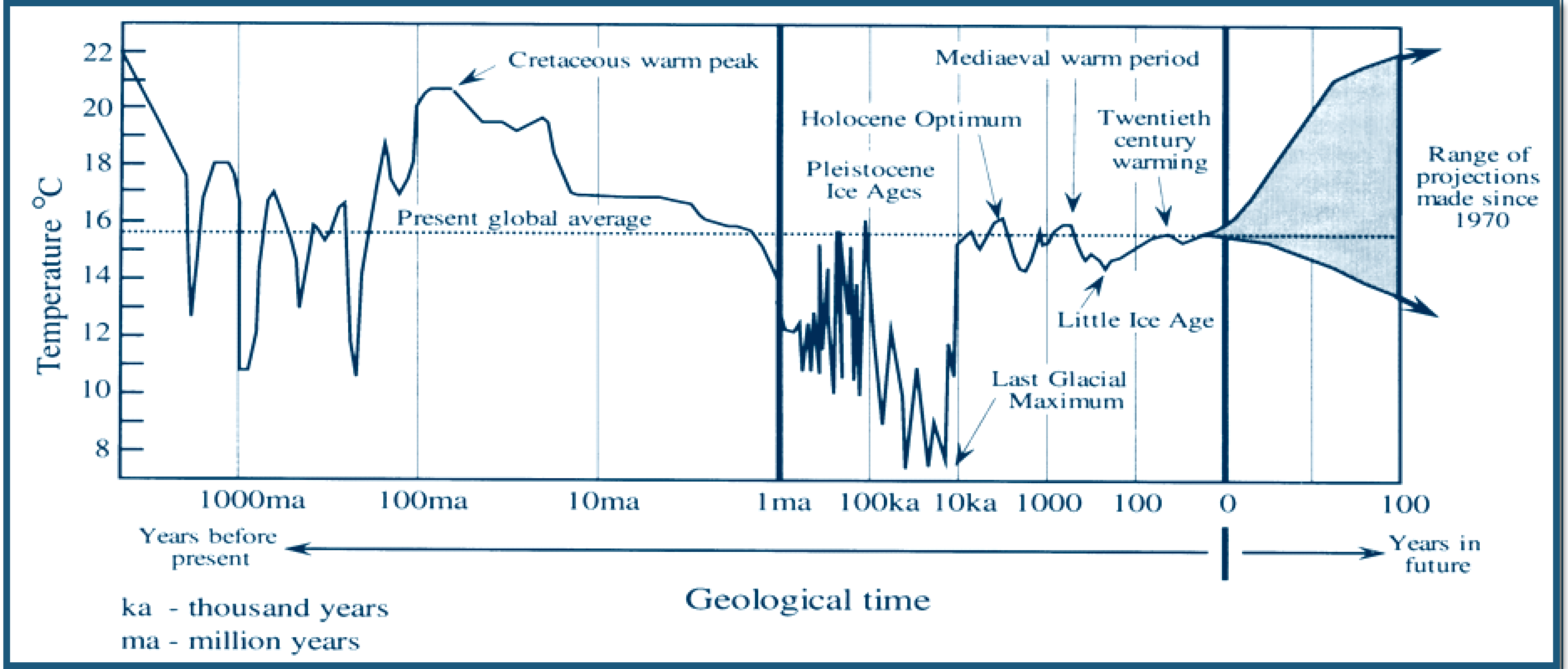
DISTINGUISHED LECTURES - 2011
SGI - SIMP - SPI

The long-term carbon cycling

- Introduction – The Earth CO2 thermostat
- Earth carbon emissions and reservoirs
- Cycling of carbon in subduction zones
- Modelling deep carbon cycling

Long term Carbon cycling
The Earth thermostat

- CO2 260 ppm 10.000 yr ago
- CO2 280 ppm in 1750

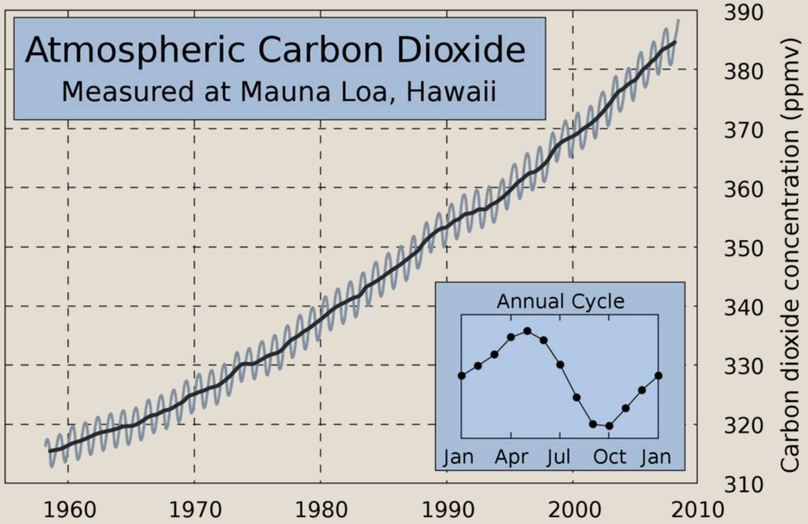


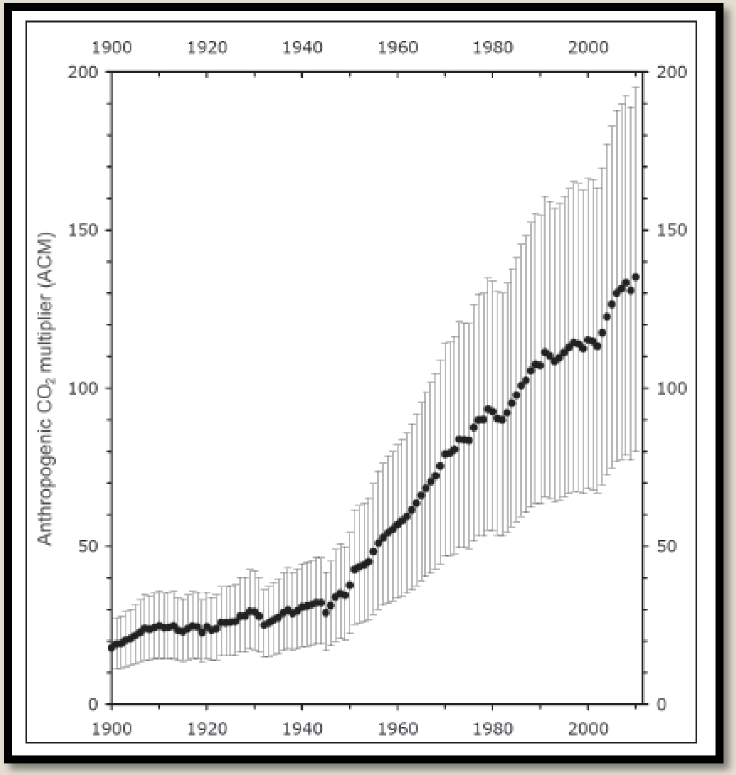
Sagan, & Mullen, 1972 Science **;** Walker, et al, 1982, *JGR.;* Zeebe, & Caldeira, 2008 Nature G; Lovelock, 1974, Tellus**;** Bryant, 1997; Archer, 2008, Nature G.

The perturbation
Anthropocene CO2 increase

Carbon Dioxide

Anthropogenic emissions	**35 GtCO2/yr or 10 Gt C/y**
Earth emissions	**0.26 GtCO2/yr (0.18-0.44Gt) or 0.1 Gt C/y**
CO2 level increase from 1750-2005	380-280=100 ppm
Conversion Rate	1 ppm= 2.12 GtC and 7.78 GtCO2
T increase of in the last 250 years	0.5 °C





Gerlach, 2011 EOS

Long-term (stable) carbon cycle

- “The irrelevance of the long-term carbon cycle to the immediate future is an important point, <u>since the global warming climate event will last for as long as it takes these slow processes to act”</u>

- …”The geologic carbon cycle sets the stage for for carbon cycle gymnastic on faster and perhaps more immediately relevant time scales”…

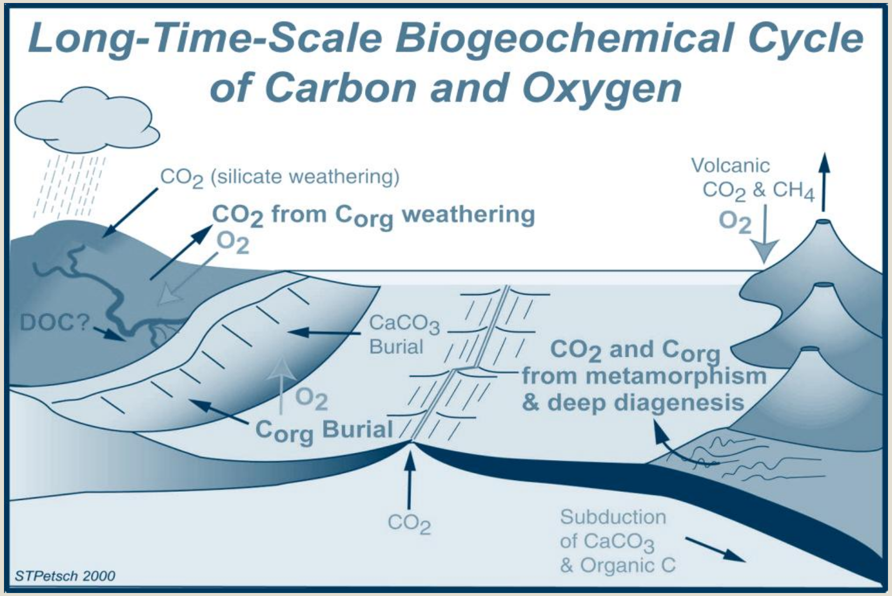
- …”**On geologic time scales the carbon cycle acts to stabilize the climate of the Earth in mysterious and wondrous ways**”…

- (ARCHER, 2010)

The long-term Earth carbon cycle

Main Reactions

- **CaSiO3 + CO2 <->CaCO3 + SiO2**
  - **(UREY, 1952)**



Silicate rock weathering

$$CO_2+CaSiO_3 \rightarrow CaCO_3 + SiO_2$$

Carbonate rock weathering

$$CO_2+H_2O+CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

Carbonate formation in oceans

$$2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + H_2O$$

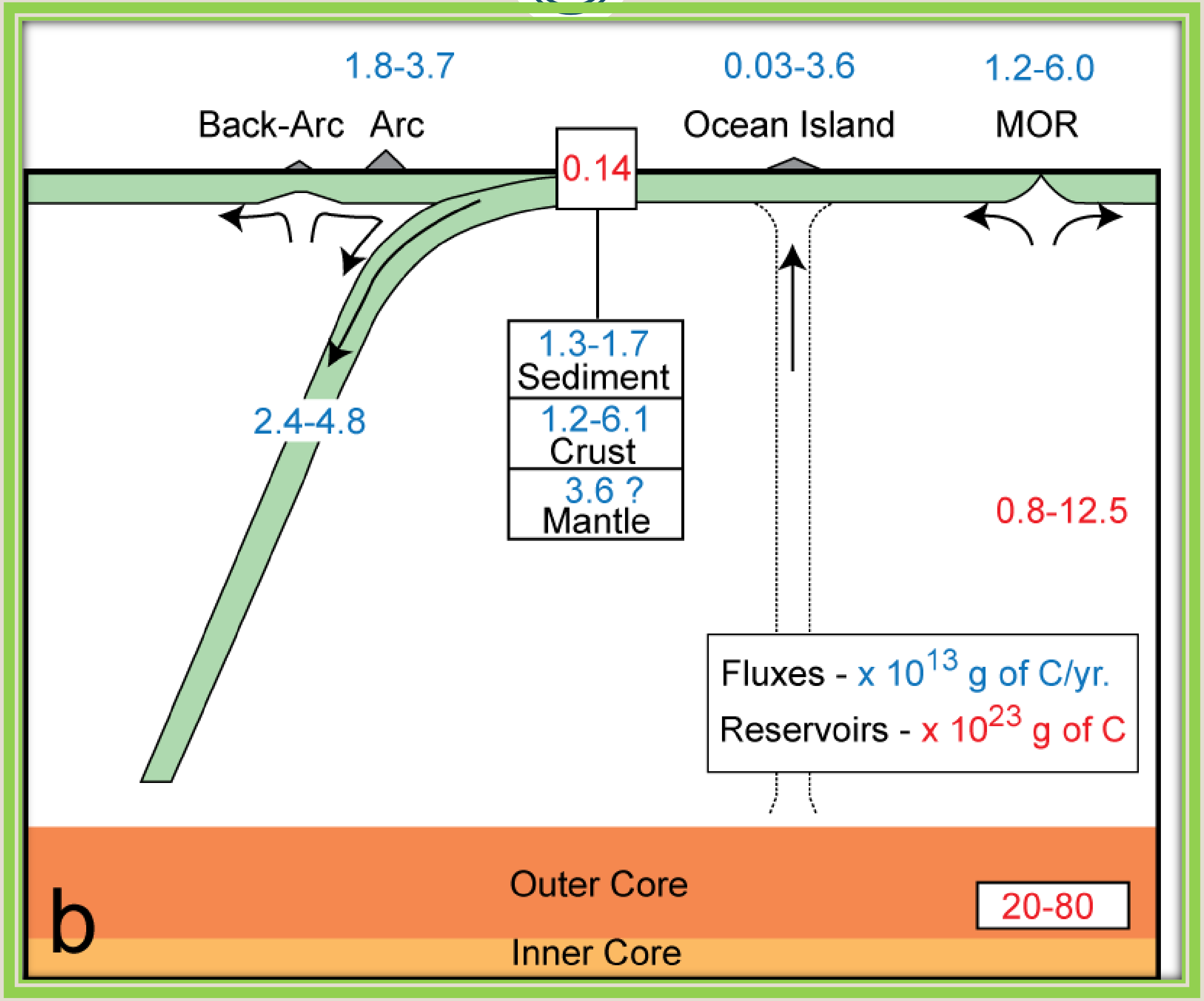
Metamorphic breakdown of carbonates

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

Melting of metamorphic carbonates

$CaCO_3 \rightarrow CO_3^{2-}$ in silicate melts

Earth Carbon reservoirs and fluxes



Dasgupta & Hirschmann, 2010 EPSL

Earth CO2 degassing
Point source measurements

Earth CO2 degassing

1970 – 1992

VOLCANIC CO_2	SUB AERIAL Mt/y	SUB AQUEOUS Mt/y	**Total**
Regional Measurements			
Etna crater 1976 - 1985 (Italy) *Allard, 1991*	25.5		
Augustine crater (Alaska, USA) *Gerlach 1991*	2.2		
Mt. St. Helens crater (Washington, USA) *Gerlach 1991*	1.8		
Nyiragongo crater (Zaire) *Le Guern, 1987*	1.2		
White Island crater (New Zealand) *Rose et al., 1986*	0.66		
Kilauea crater (Hawaii, USA) *Greenland et al., 1985*	0.47		
Vulcano crater (Italy) *Baubron et al., 1990*	0.06		
Erta 'Ale (Etiopia) *Le Guern et al., 1979*	0.02		
Mt. St. Helens 1980 eruption (USA) *Casadevall et al., 1983*	4.8 - 22		
Lake Nyos 1986 event (Cameroon) *Kousakabe et al., 1989*	1.24		
Measurements - Total 1970 - 1992			**31.9**
Measurements - Average 1992 (n=8)			**4**
Global Extrapolations*			
Le Guern, 1982	48		
Gerlach, 1991	80	22 - 40	102 - 120
Allard, 1992	66		
Marty and Le Cloarec, 1992	66 - 110		
Global Estimates§			
Williams et al., 1992	64		
Varekamp et al., 1992	145	66 - 97	
Range Global , 1970 - 1992	**48 - 145**	**22 - 97**	**70 - 242**

Frezzotti et al., 2010. JVE

VOLCANIC CO_2	SUB AERIAL Mt/y	SUB AQUEOUS Mt/y
Regional Measurements		
Pinatubo 1991 eruption (Philippines) *Gerlach et al., 1996*	42	
Popocatépetl crater (Mexico) *Varley and Armienta, 2001*	21.9	
Etna crater 1993 - 1997 (Italy) *Allard, 1998*	4 - 13	
Masaya Caldera diffuse (Nicaragua) *Pérez et al., 2000*	10.5	
Etna flanks (italy) *D'Alessandro et al., 1998*	0.6 - 6	
Oldoinyo Lengai crater (Tanzania) *Koepnick, 1995*	2.2 - 2.6	
Stromboli crater (Italy) *Allard et al., 1994*	1 - 2	
Masaya crater (Nicaragua) *Burton et al., 2000*	0.8 - 1.13	
Cerro Negro total (Nicaragua) *Salazar et al., 2001*	1	
Rabaul Caldera (Papua N.G.) *Perez et al., 1998*	0.88	
Erebus crater (Antarctica) *Wardell and Kyle, 2003*	0.7	
Redoubt crater (Alaska, USA), *Casadevall et al., 1994*	0.7	
Canadas Caldera (Tenerife, Spain) *Hernadez et al., 2000a*	0.2	
Teide flanks (Tenerife, Spain) *Salazar et al., 1997*	0.2	
Vulcano fumaroles (Italy) *Italiano et al., 1998*	0.13	
Usu crater (Japan) *Hernandez et al., 2001*	0.04 - 0.12	
Mout Baker crater (Washigton, USA) *Mc Gee et al., 2001*	0.07	
Stromboli flanks (Italy) *Carapezza and Federico, 2000*	0.07 - 0.09	
Hakkoda flanks (Japan) *Hernandez et al., 2000b*	0.04	
Measurements - Total 1992 - 2002	**83 - 90.3**	
Measurements - Total 1970 - 2002	**114.9 - 122.2**	
Average 1970 - 2002 (n=24)	**4.6 - 4.7**	

NON-VOLCANIC CO_2	SOIL EMISSION Mt/y (km2)
Regional Measurements	
Back arc Pacific Rim, *Seward and Kerrick, 1996*	44
Central Apennine (Italy) *Chiodini et al., 2000*	4 - 13 (12,000)
Larderello and Amiata (Italy) *Chiodini et al. 2000*	2.2
Indonesia - Philippines, *Seward and Kerrick, 1996*	1.8
Nisyros soil (Greece) *Brombach et al., 2001*	0.8
Siena basin (Italy) *Etiope et al., 1996*	0.5 (200)
Taupo volcanic zone (N Zealand) *Seward and Kerrick, 1996*	0.44
Cascade Range (Oregon, USA) *James et al., 1999*	0.4
St. Andreas fault (California, USA) *Lewicki and Brantley, 2000*	0.3 (60)
Ustica (Italy) *Etiope et al., 1999*	0.26 (9)
Mammoth Mountain (California, USA) *Rahn et al., 1996*	0.15 (0.4)
Yellowstone (Wyoming, USA) *Werner et al., 2000*	0.18 (3.5)
Measurements - Total 1992 - 2002	**55 - 64**

1992 - 2010

Global Extrapolations*				**Total**
Brantley and Koepenick, 1995	88 - 132			
Kerrick, 2001	88 - 110			
Morner and Etiope , 2002	300		> 600	900
Kerrick and Caldeira, 1998			44	
Global Estimates§				
Sano and Williams, 1996	136	44 - 132		
Marty and Tolstikhin, 1998	242	57 -136		367
Range, 2002	**110 - 242**	**44 - 136**	**600**	**367 - 900**

Frezzotti et al., 2010. JVE

Measurements of natural point source emissions

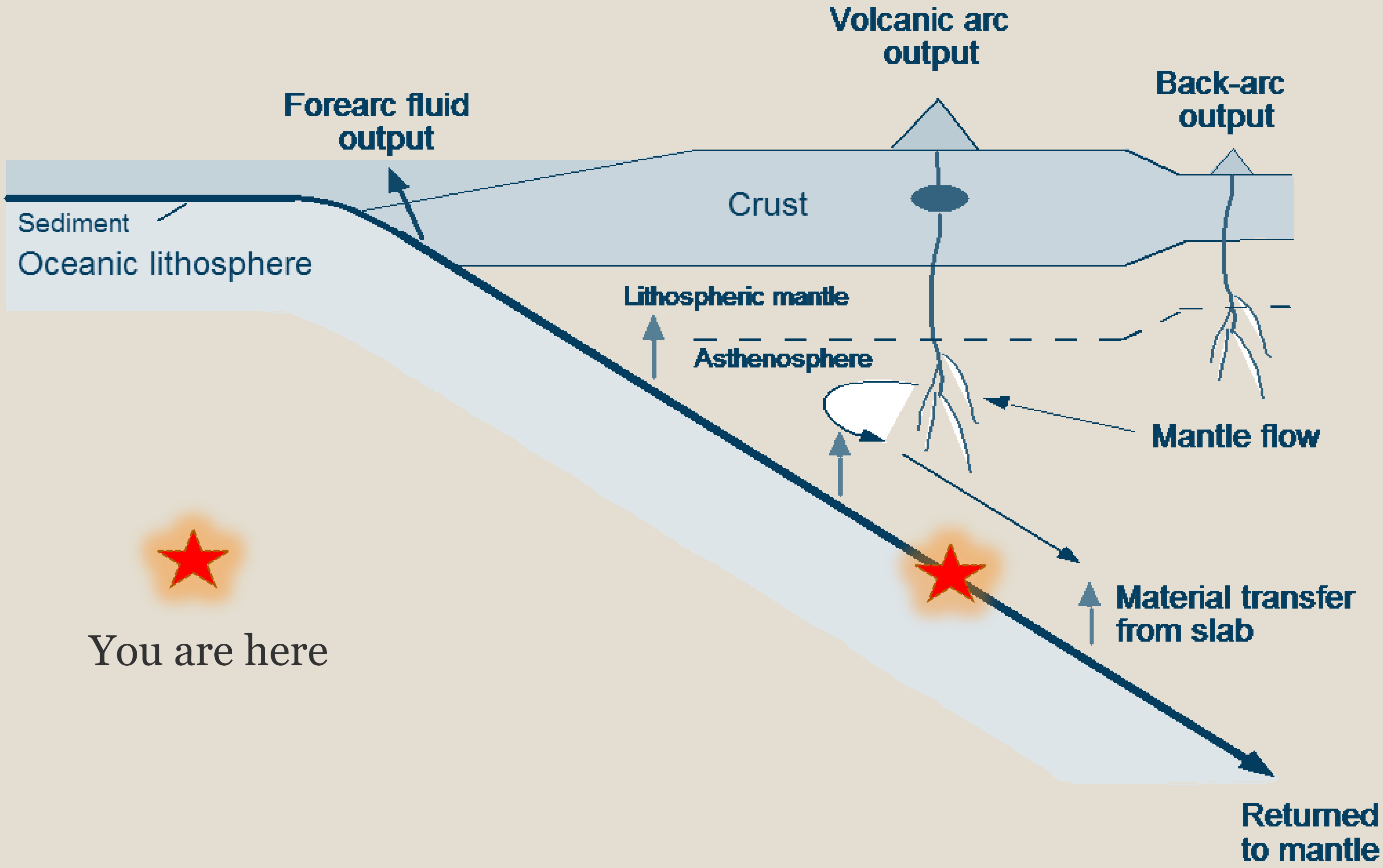
- From a total atmospheric CO2 of 0.01 % in the 1990's up to 0.1 % in the 2000's of the anthropogenic emissions.

- the CO2 emission rates from single volcanoes can be highly variables, differing of one or two orders of magnitude.

- Such a constantly increasing trend in a frame were the degassing processes are unknown indicates that the natural Earth's emissions are unquantified.

- The reasons behind variations between different volcanoes are unknown.

From Volcanology to Petrology
Deep cycling of Carbon



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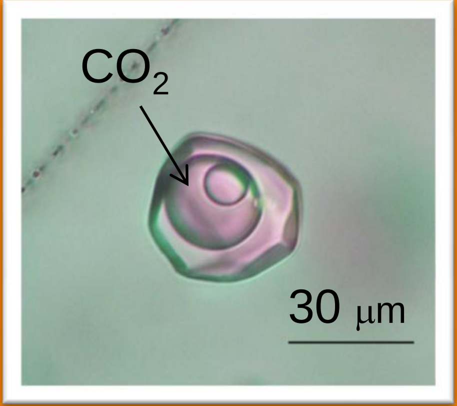
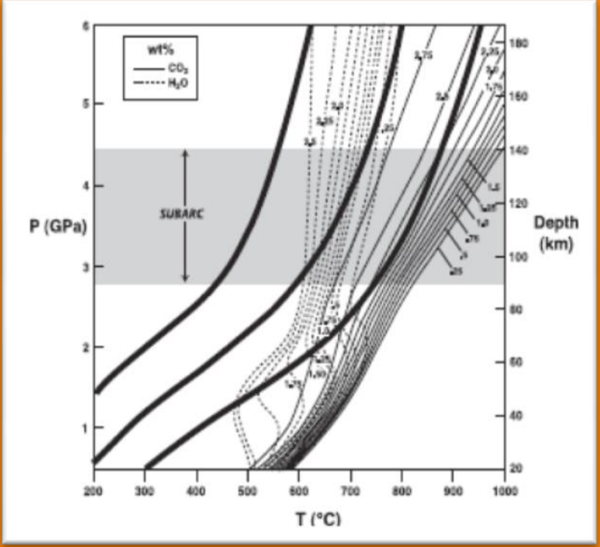
How do we model C fluxes during subduction?

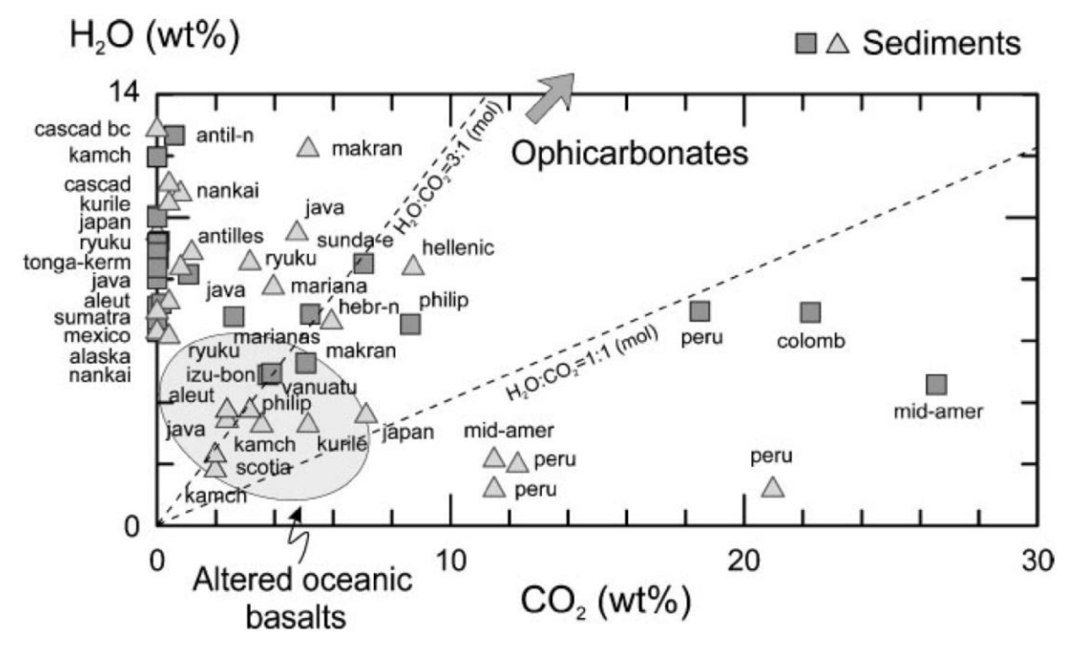
- Fluid inclusions
- HP metamorphic rocks
- Experimental petrology





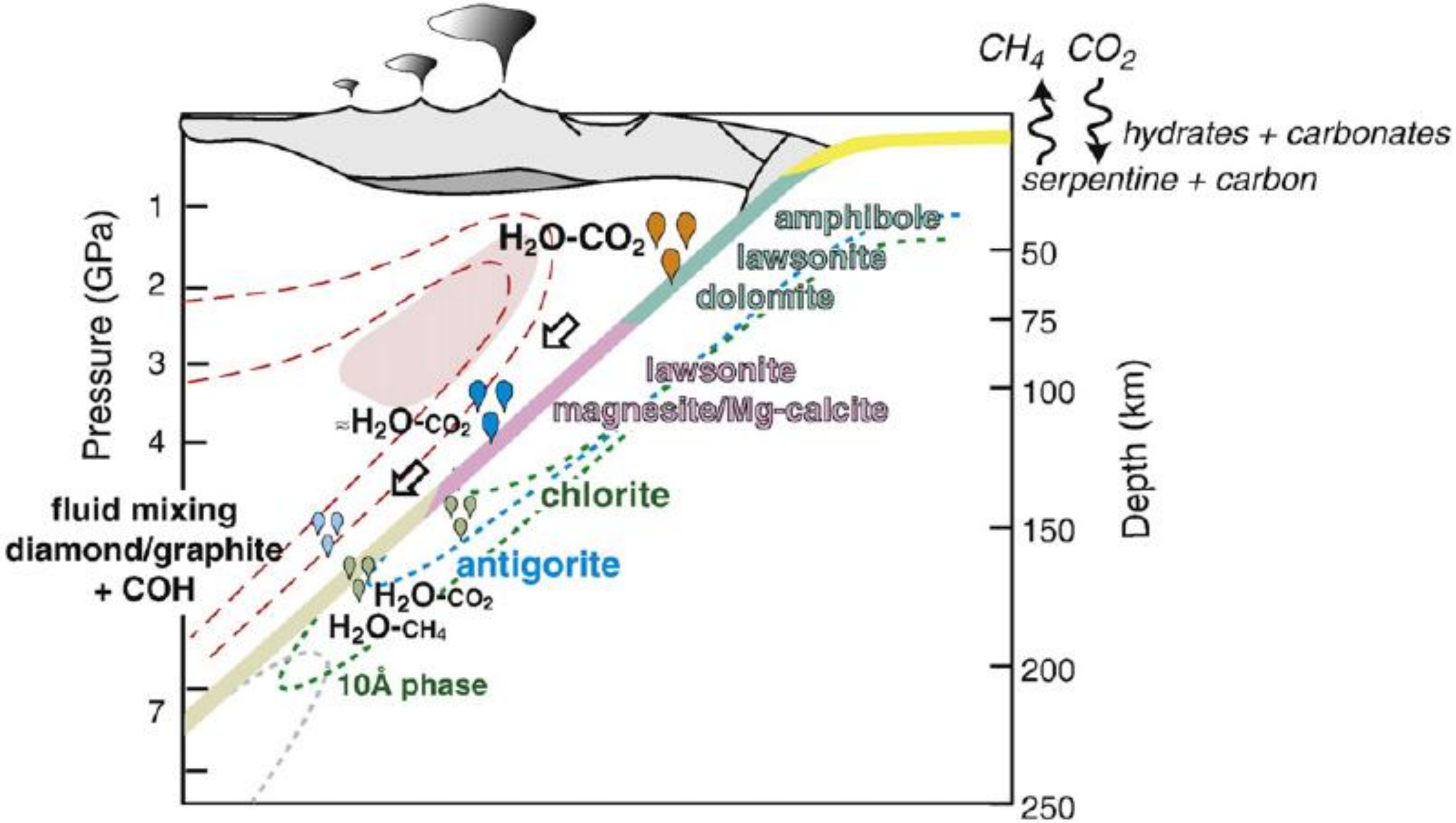
Subducted Carbon

- Oceanic metabasalts (41 x Mt/yr)
- Ocean floor sediments (24 x Mt/yr)



Schmidt and Poli, 1998 EPSL

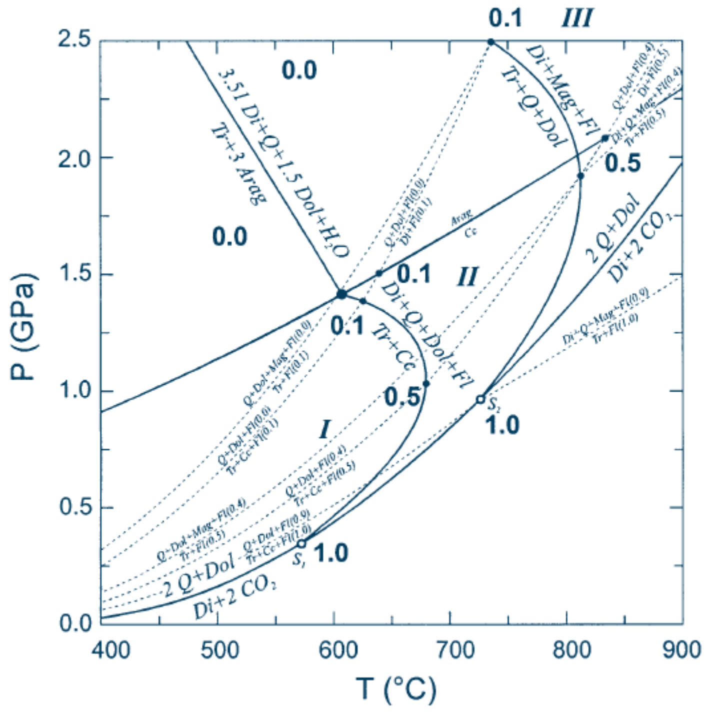
Carbon release from slab

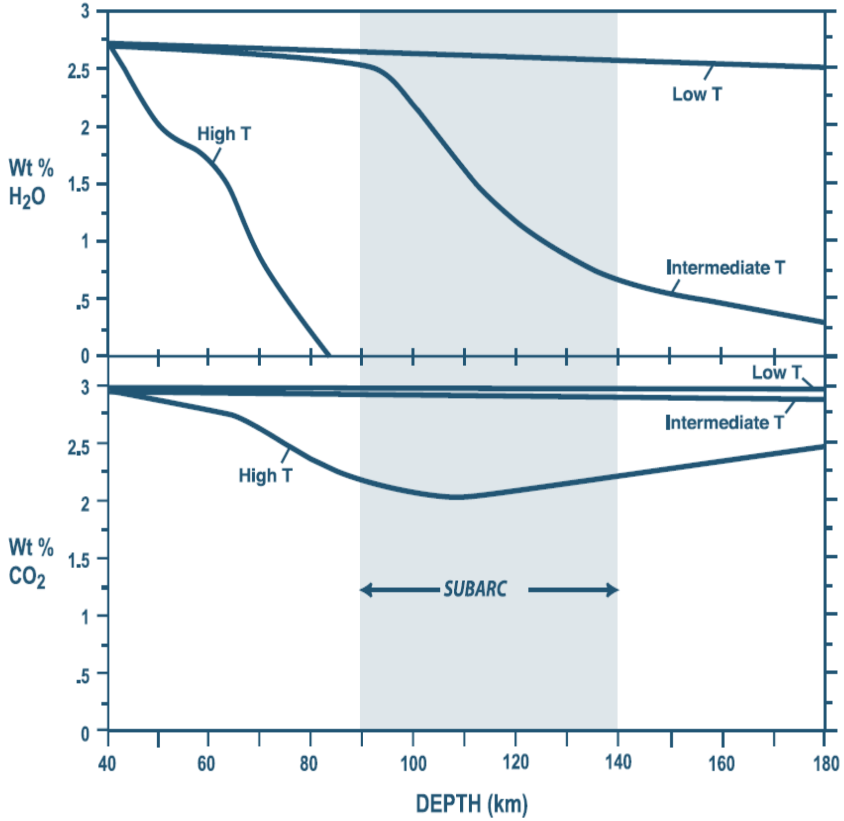


Poli et al., 2009 EPSL

Metamorphic breakdown of carbonates

$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$





Molina & Poli, 2000 EPSL

Kerrick & Connolly, 2001 EPSL

Subduction -Volcanic degassing CO2 imbalance

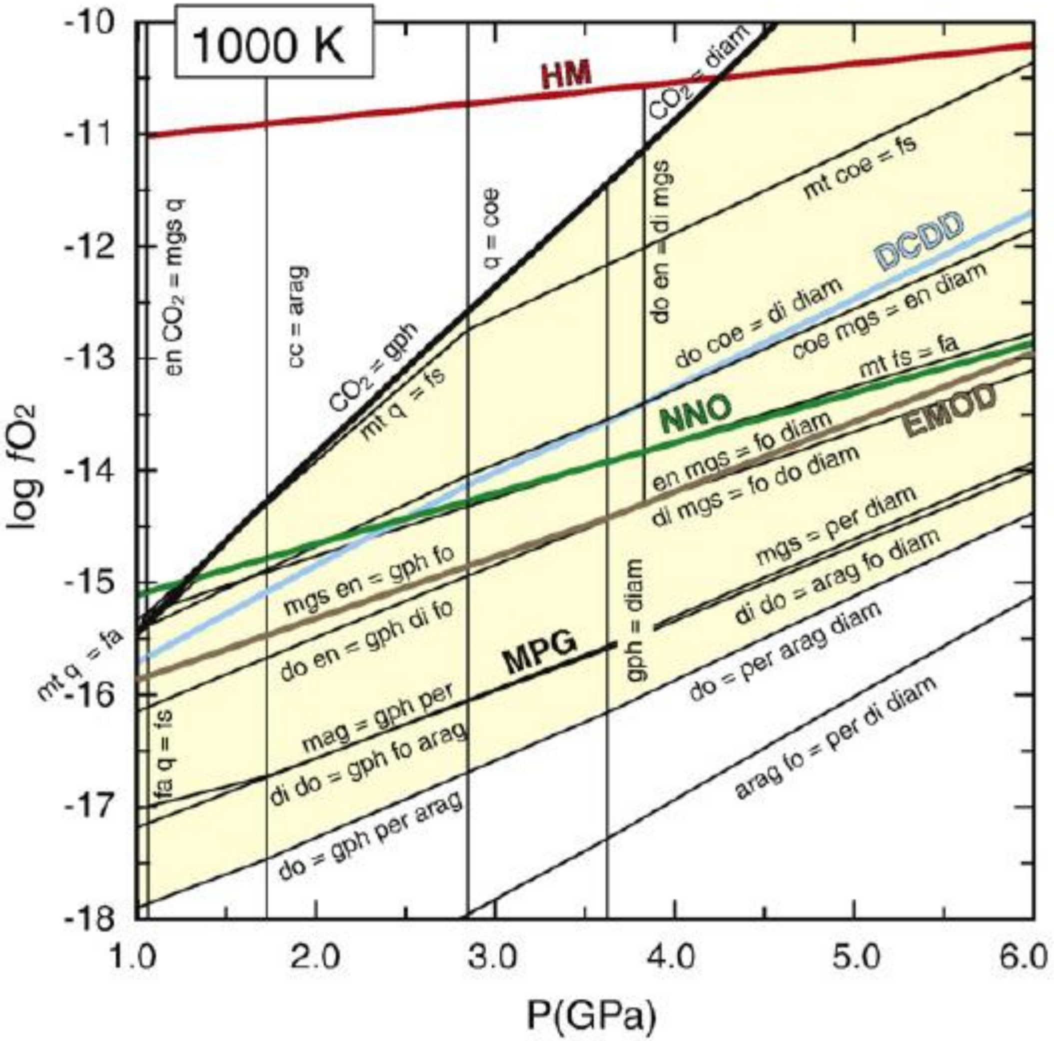
Decarbonation of the subducted slab is generally limited, since it requires higher T than most subduction slabs.

HOWEVER

Observations of CO_2 flux and inferences based on $CO_2/^3He$ in volcanic gases lead to the conclusion that about half of the CO_2 flux from volcanoes comes from arc volcanism, and that 80% of this is recycled from subducted materials.

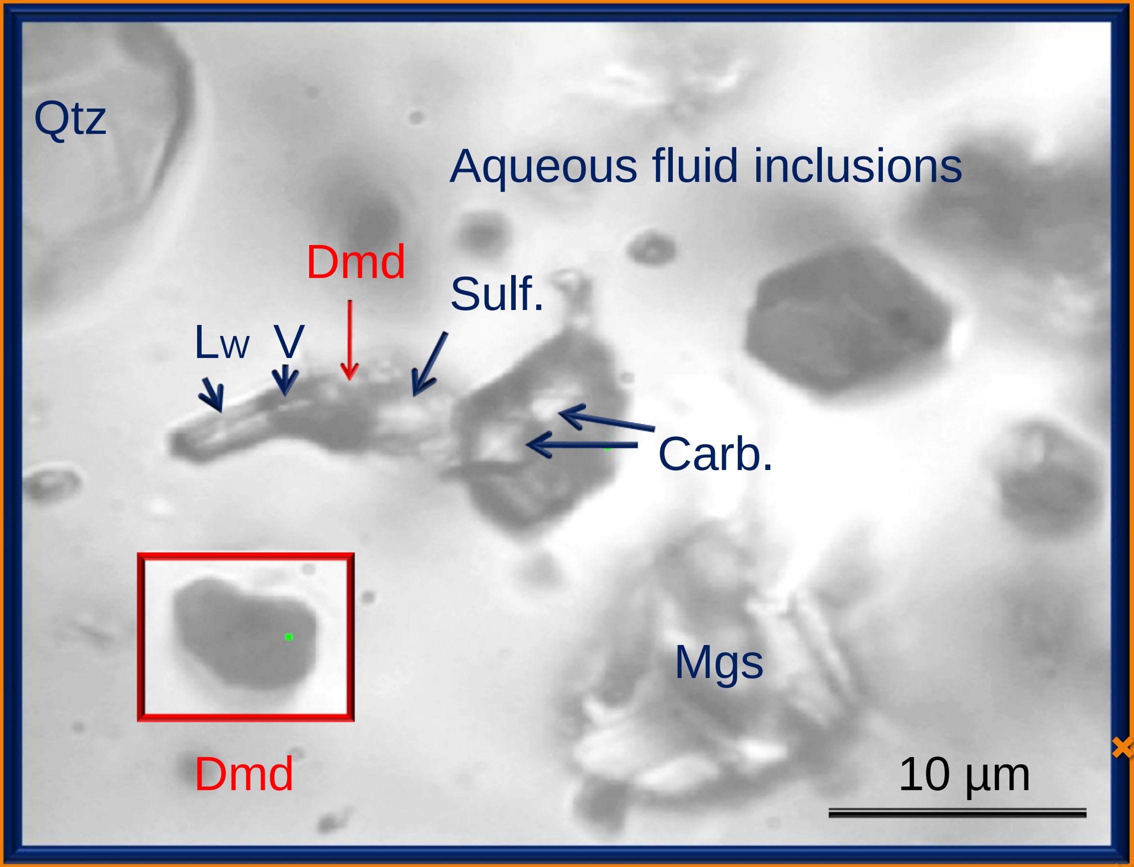
Marty and Tolstikhim (1998) CG; Molina and Poli (1998) EPSL; Kerrick and Connolly (2001) N; Sano and Williams EPSL (1996)

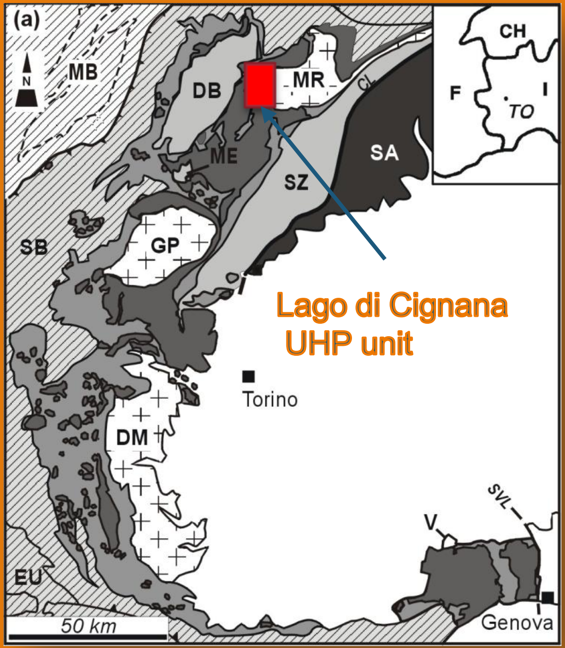
fO2 control on Carbon speciation during subduction



Poli et al., 2009 EPSL

Microdiamonds in UHP rocks (W Alps)





- Segment of former oceanic crust
- Eclogite facies metabasics and metasediments

Most diamond inclusions < 10 µm

Most diamonds within fluid inclusions ≤ 1 µm

Frezzotti et al., 2011 NatureG

Subduction fluids

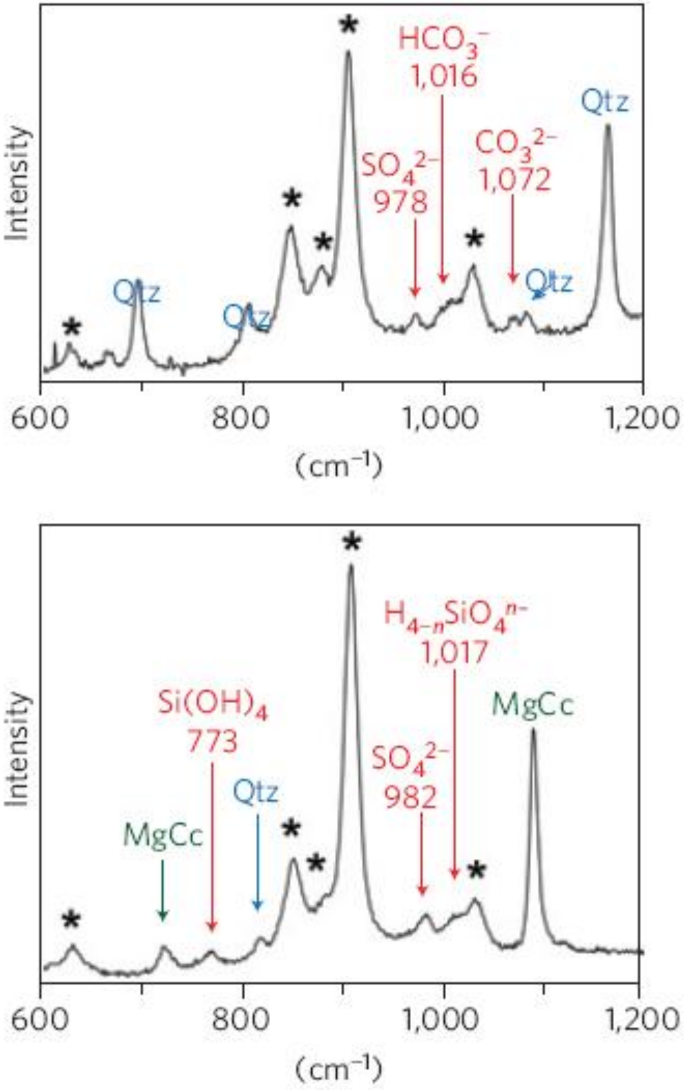
HCO_3^- > 0.016 mol/kg H_2O

SO_4^{2-} > 0.002 mol/kg H_2O

CO_3^{2-} > 0.006 mol/kg H_2O

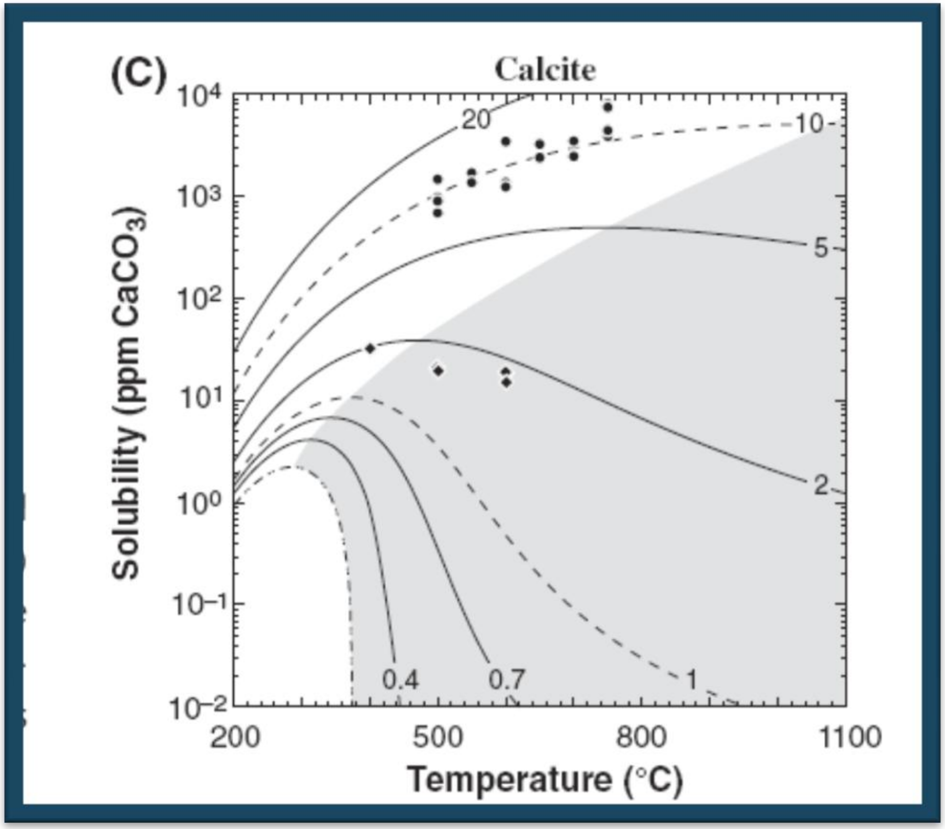
Raman spectra collected in liquid water contained within fluid inclusions

Excitation spot 1x1x5 µm



Frezzotti et al., 2011 NatureG

carbon release from the slab through dissolution

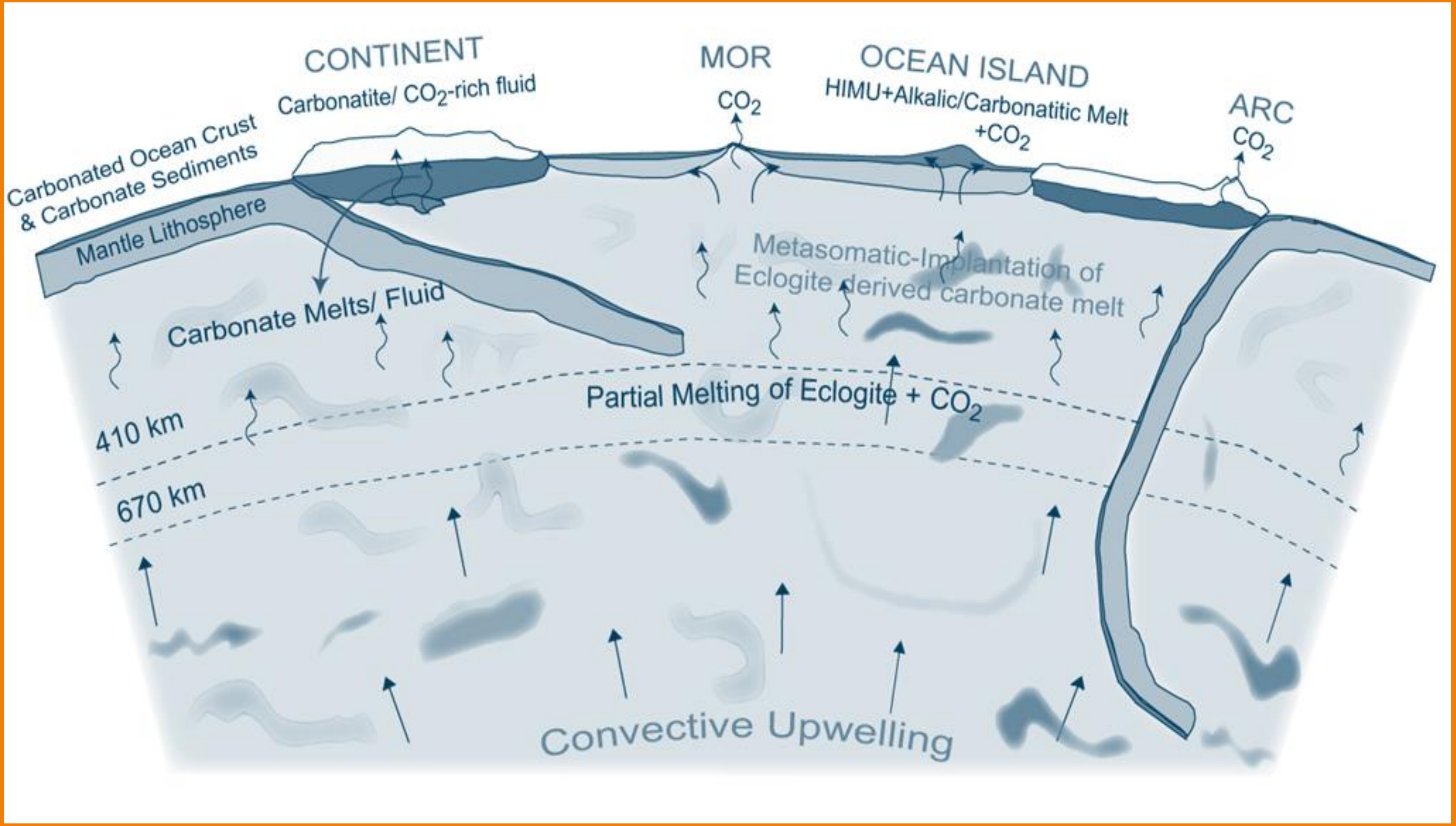


Subduction fluids

(T= 600°C; P= 3.4 GPa, or 120 km)

Doljes and Manning, 2010, Geofluids

Deep cycling of Carbon



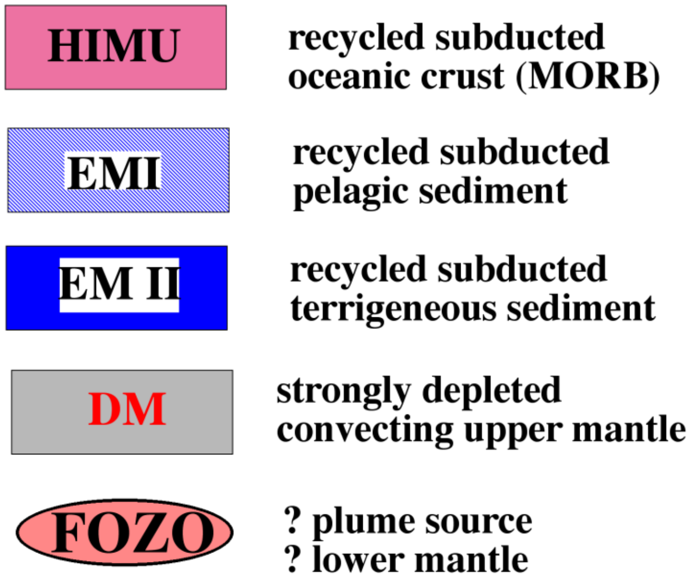
Mantle composition

- Scale lengths of heterogeneities (metasomatism)
- Does recycled oceanic crust remain distinct & for how long
- Chemical modifications introduced by plate subduction plus delamination of continental lithospheric roots
- Role of CO_2 v H_2O in mantle melting

Morb - OIB

Present-day mantle reservoirs
The MORB-OIB spectrum

Virtually all the geochemical end-members can be explained by an origin from mantle sources that have experienced interaction with crustal “material” introduced at depth.

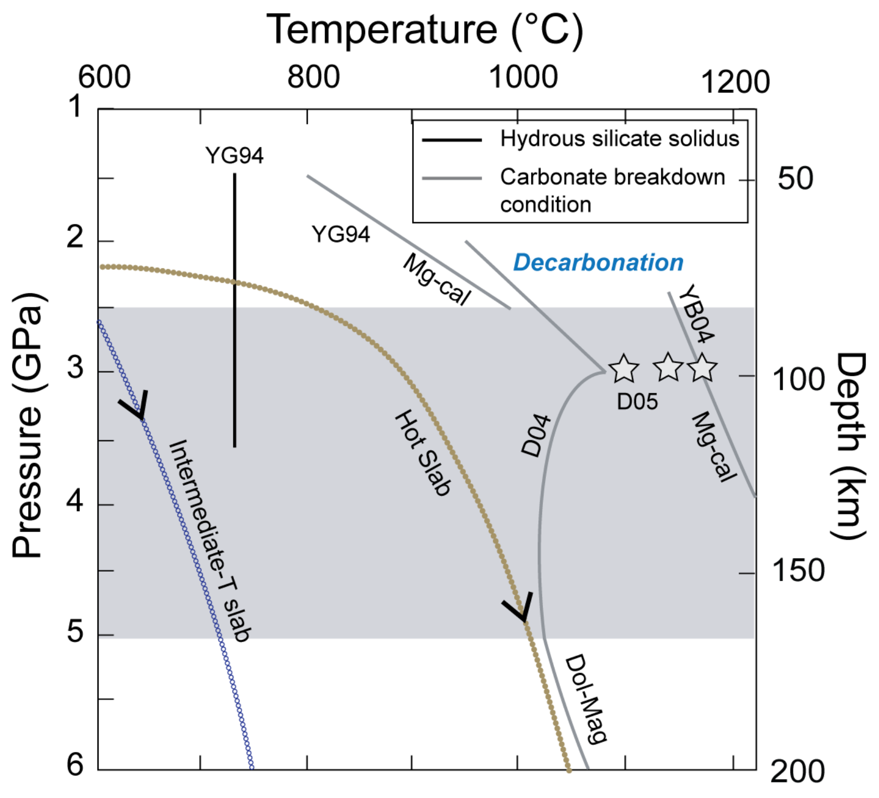


HIMU	**recycled subducted oceanic crust (MORB)**
EMI	**recycled subducted pelagic sediment**
EM II	**recycled subducted terrigeneous sediment**
DM	**strongly depleted convecting upper mantle**
FOZO	**? plume source** **? lower mantle**

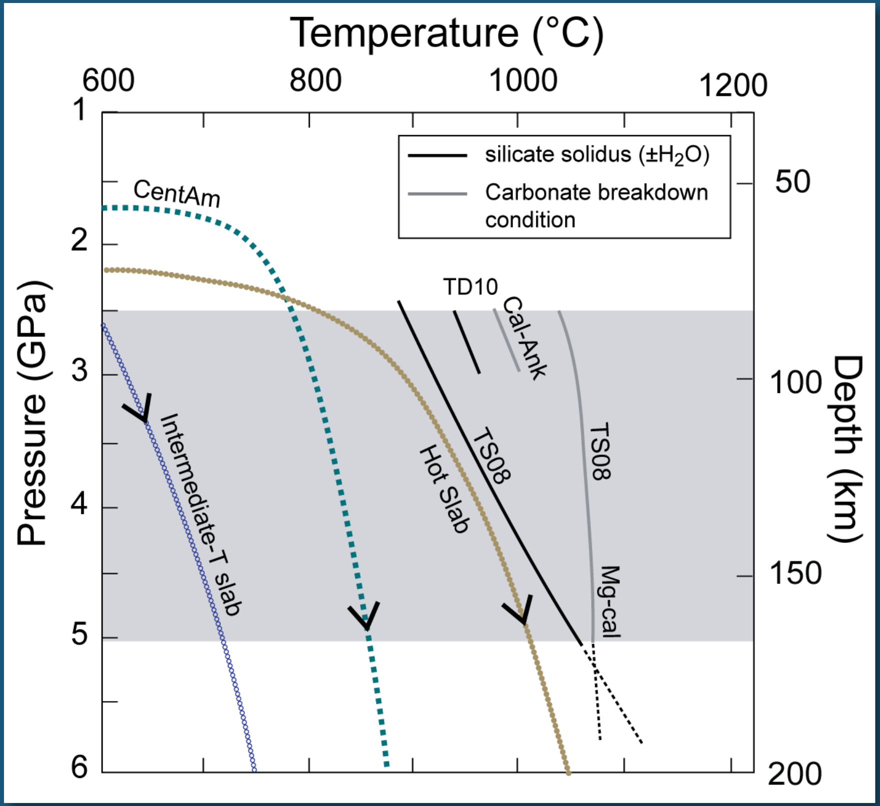
Wilson, 2005

Melting of carbonated rocks

Carbonated basalts

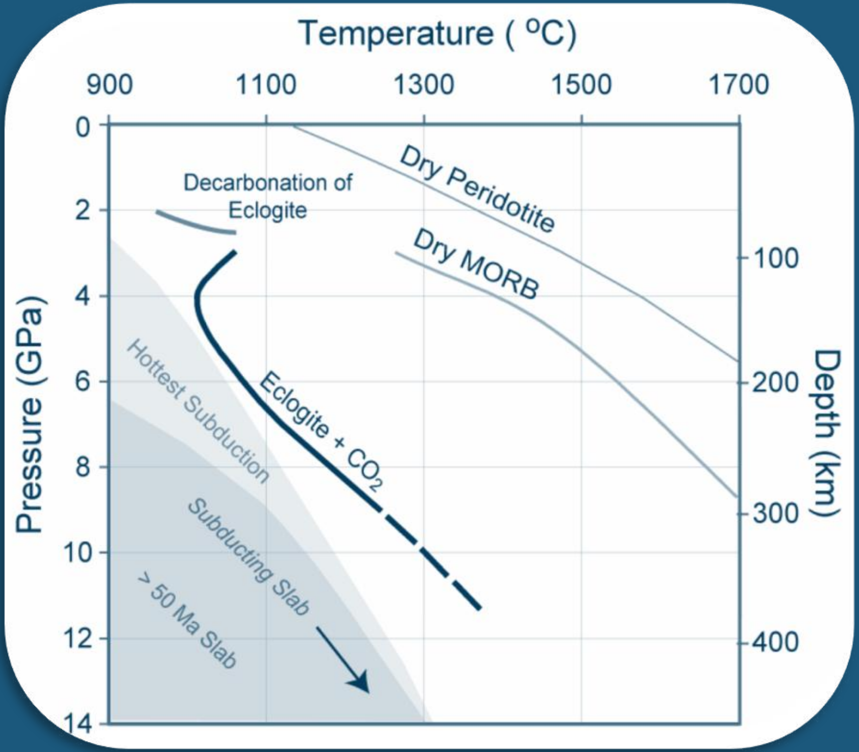


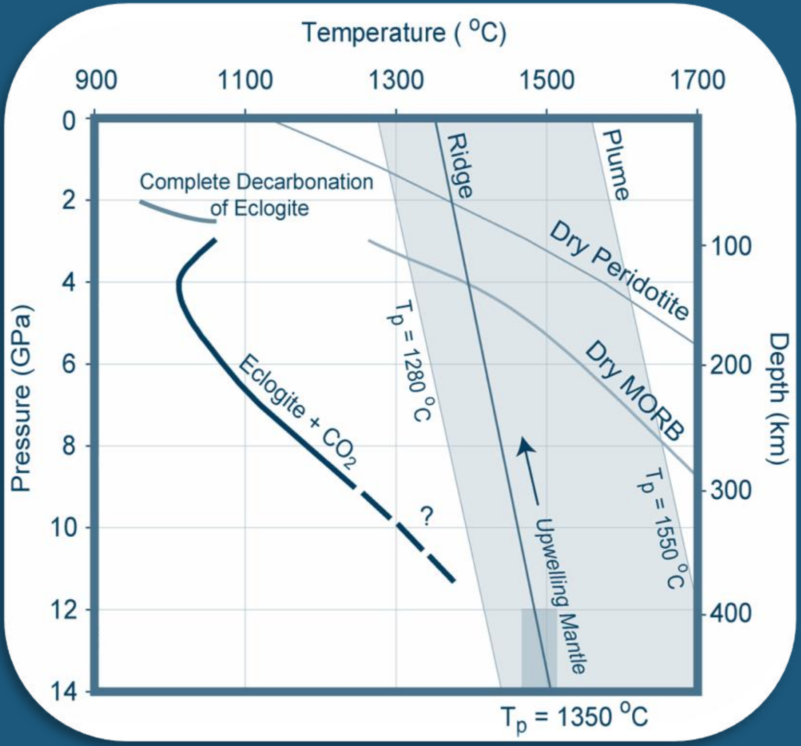
Carbonated sediments



(Yaxley and Green, 1994; Yaxley and Brey, 2004; Tsuno and Dasgupta, 2010; Dasgupta et al., 2004, 2005; Thomsen and Schmidt, 2008;)

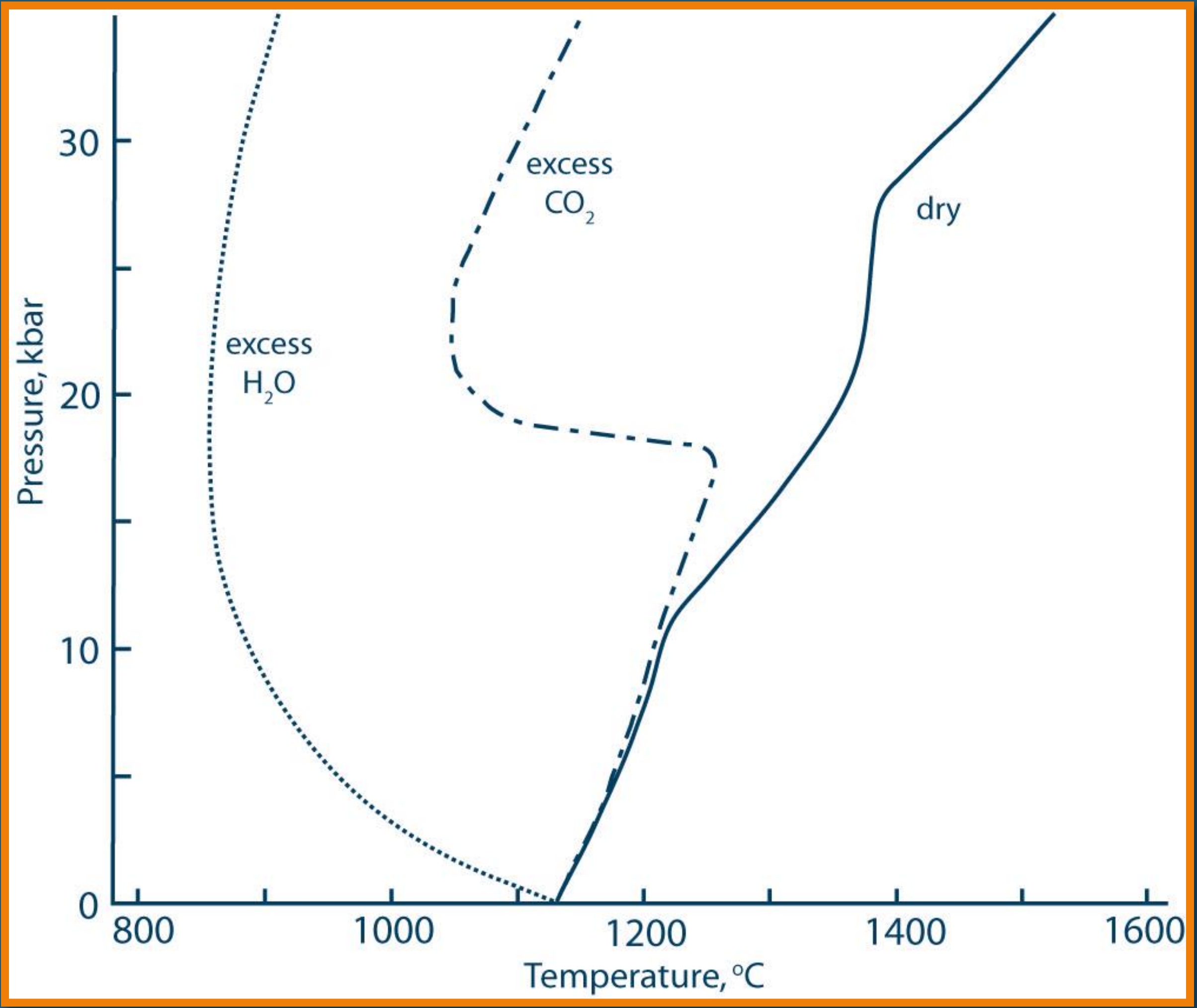
Melting of carbonated eclogite



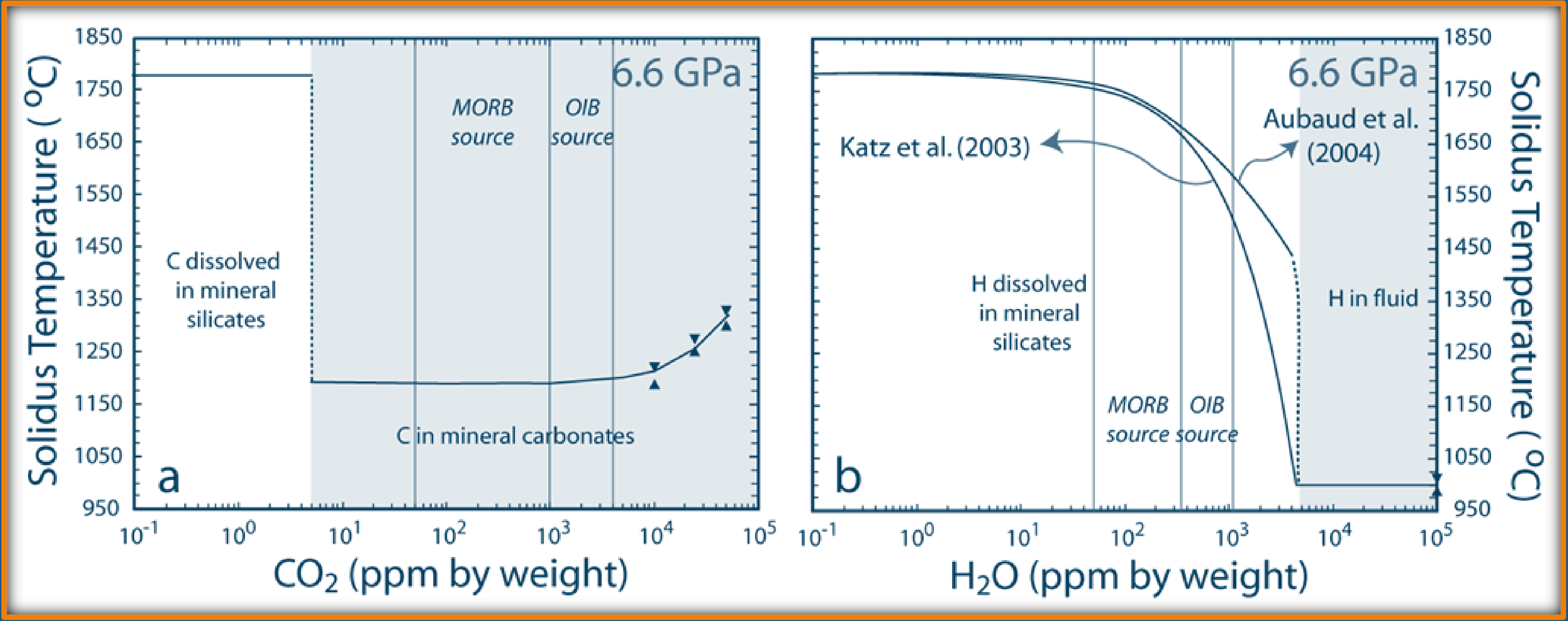


Dasgupta et al. (2004) - EPSL

Peridotite solidus

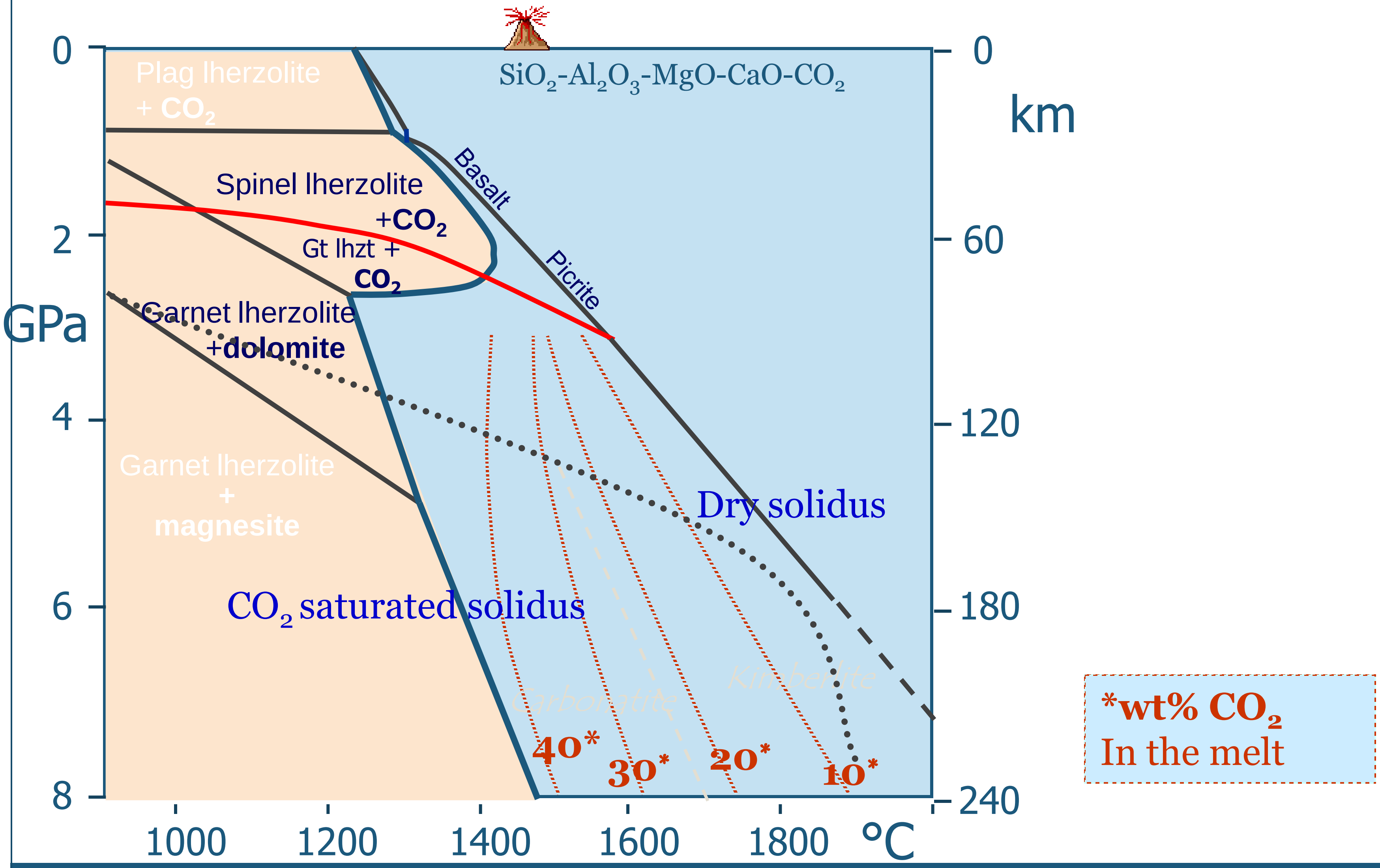


Peridotite Solidus – H2O and CO2



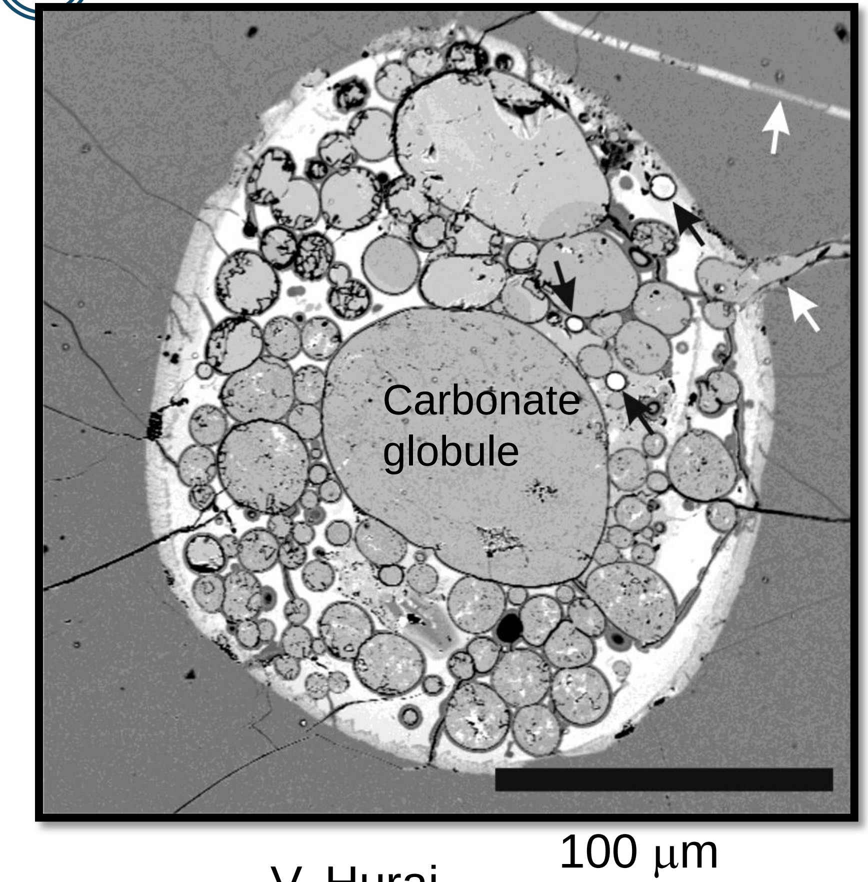
Dasgupta & Hirschmann , 2007) - AmMin

Transition from carbonate melts to carbonated silicate melts



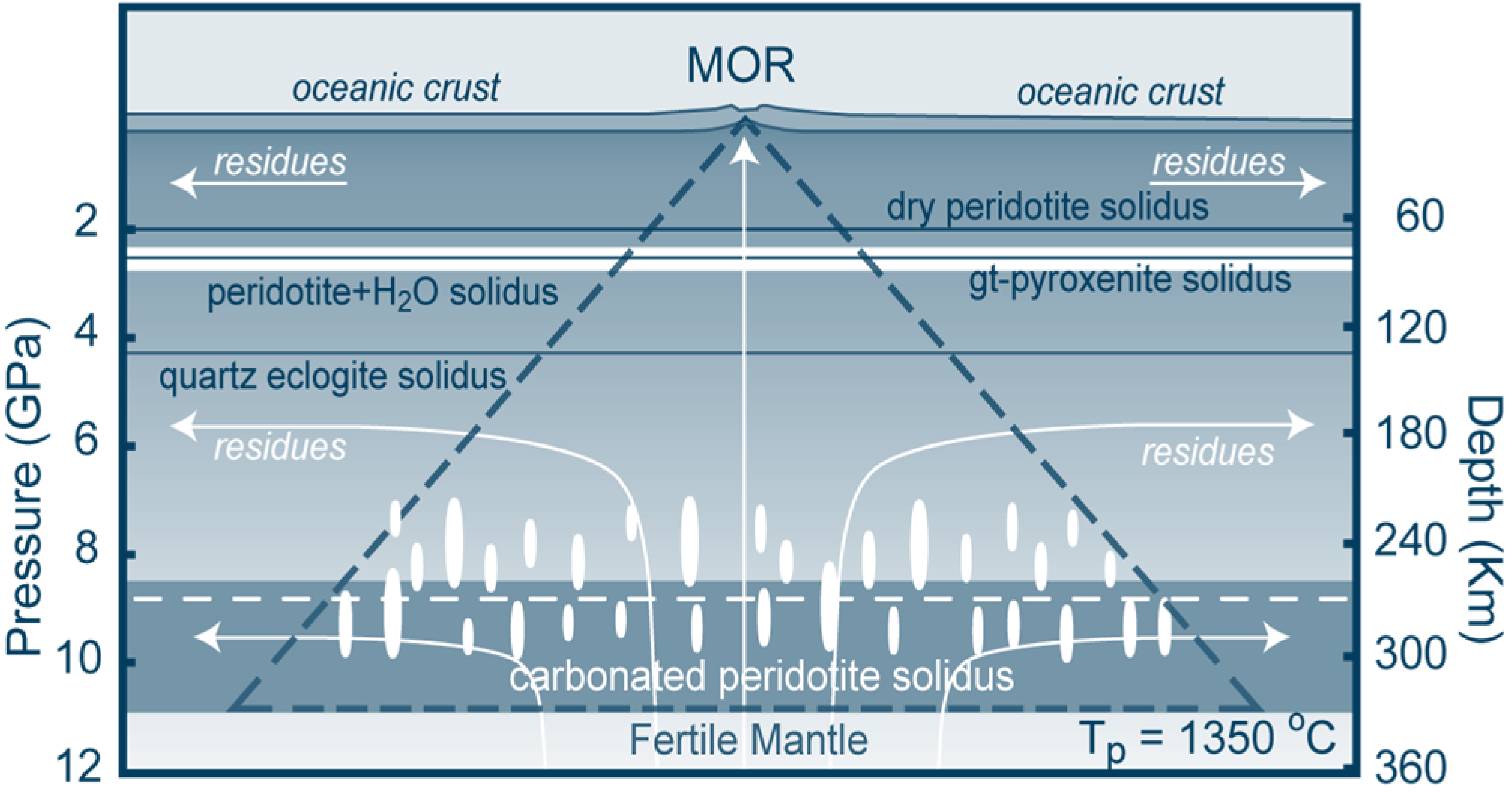
Modified from Gudfinnsson and Presnall (2005)

Carbonate globules in mantle rocks



V. Hurai

Fluxes of mantle CO2 between 120 - 3,400 Mt/yr beneath mid ocean ridges (MOR).



Dasgupta & Hirschmann (2006) Nature

Deep Carbon cycling beneath Italy

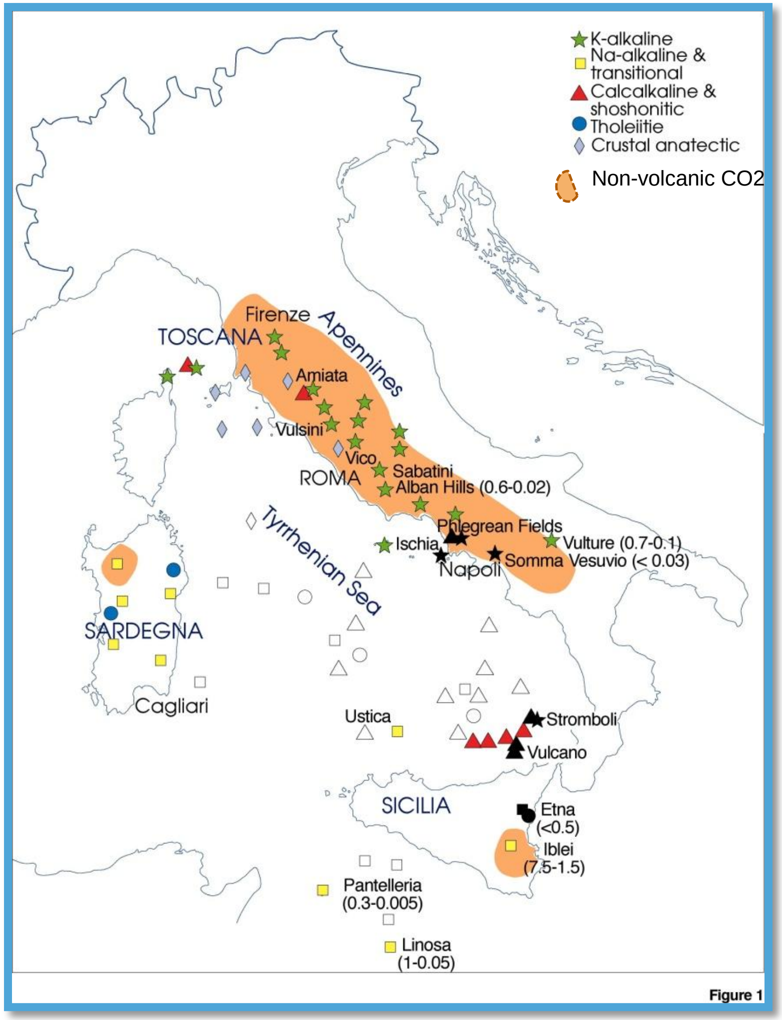


Figure 1

Geologic CO_2 degassing in Italy

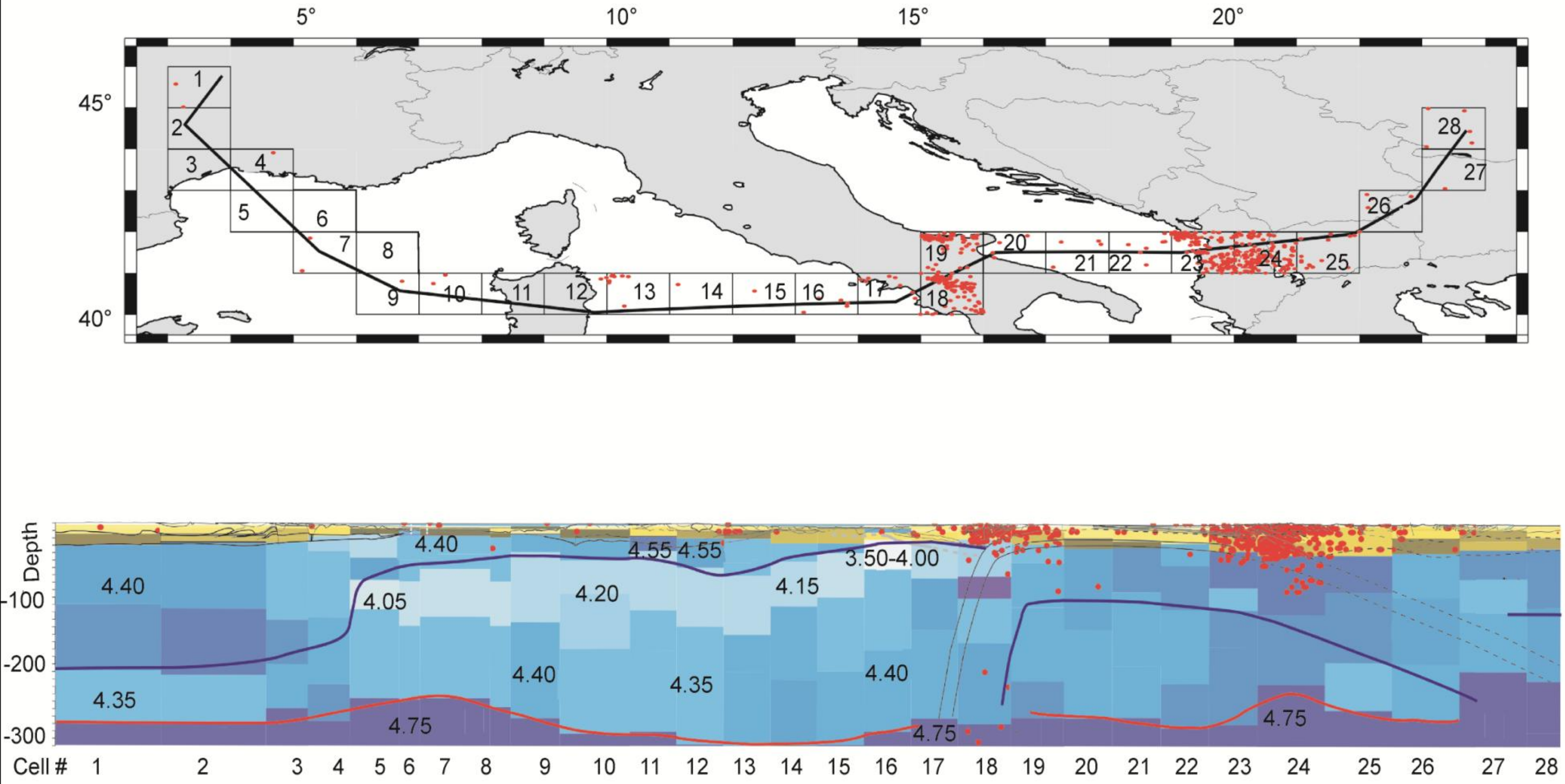
Volcanic	**Output (Mt/y)**
Crater emission	
Etna (1976 - 1985)[1, 2]	25.5
Etna (1993 - 1997)[3]	4 - 13
Stromboli[4]	1 - 2
Vulcano[5]	0.066
Ground emission	
Vulcano Fossa crater[6]	0.073
Vulcano plains[7]	0.027
Vulcano fumaroles[8]	0.088
Stromboli[9]	0.07 - 0.09
Vesuvio[10]	0.5
Solfatara, Phl. Fields[11]	1.8
Ischia[12]	0.14

Non-volcanic	**Output (Mt/y)**
Regional	
Central Italy[13]	> 4
Central Apennines[14]	4 - 13.2
Tuscany and N Latiun	6
Campania[15]	3
Central Italy[16]	9.7 - 17
Soil degassing	
Latera, Vulsini[13]	> 0.07
Alban Hills[16]	0.2
Siena graben[17]	> 0.5
Ustica[18]	0.02
Gas vents	
Mefite d'Ansanto[13]	0.3
Rapolano, Tuscany[15]	0.035
Mofeta dei Palici, Sicily[19]	0.091
Geothermal Fields	
Mt. Amiata[20]	0.5

1) Allard et al., 1991; 2) Gerlach, 1991; 3) Allard, et al., 1998; 4) Allard et al., 1994; 5) Baubron et al., 1990
6) Chiodini et al., 1996; 7) Chiodini et al., 1997; 8) Italiano et al., 1998; 9; Carapezza and Federico, 2000
10) Frondini et al., 2004; 11) Caliro et al., 2008; 12); Aiuppa et al., 2007; 13) Rogie et al., 2000;
14) Chiodini et al., 2000; 15) Chiodini et al., 2004; 16) Gambardella et al., 2004; 17) Etiope, 1995;
18) Etiope et al., 1999; 19) Di Gregorio et al., 2002; 20) Frondini et al., 2008

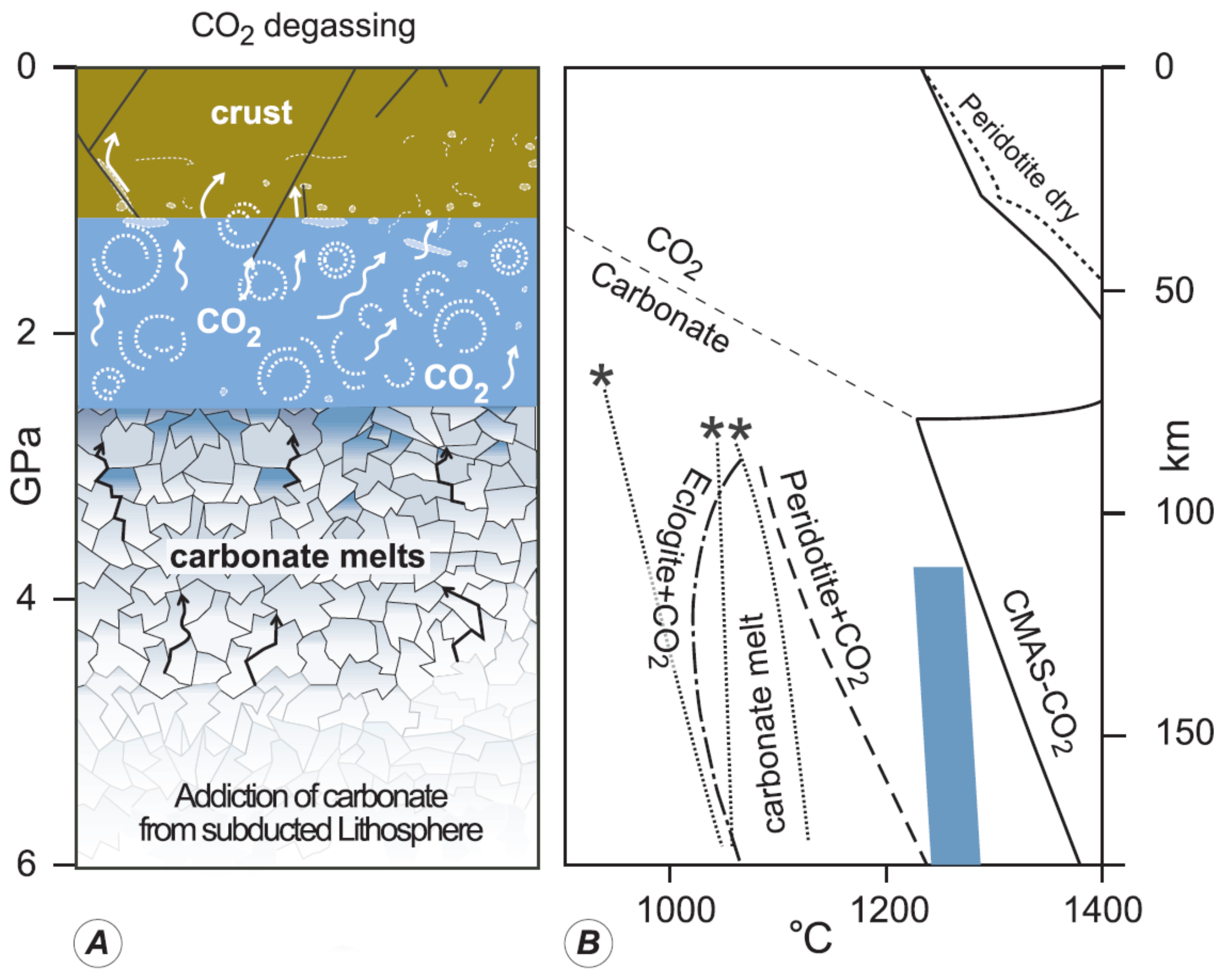
Frezzotti et al., 2009 Chem Geol

Section 1



Panza et al., 2007 ES Review

Carbon degassing beneath western Mediterranean region



Frezzotti et al., 2009, Chem Geol

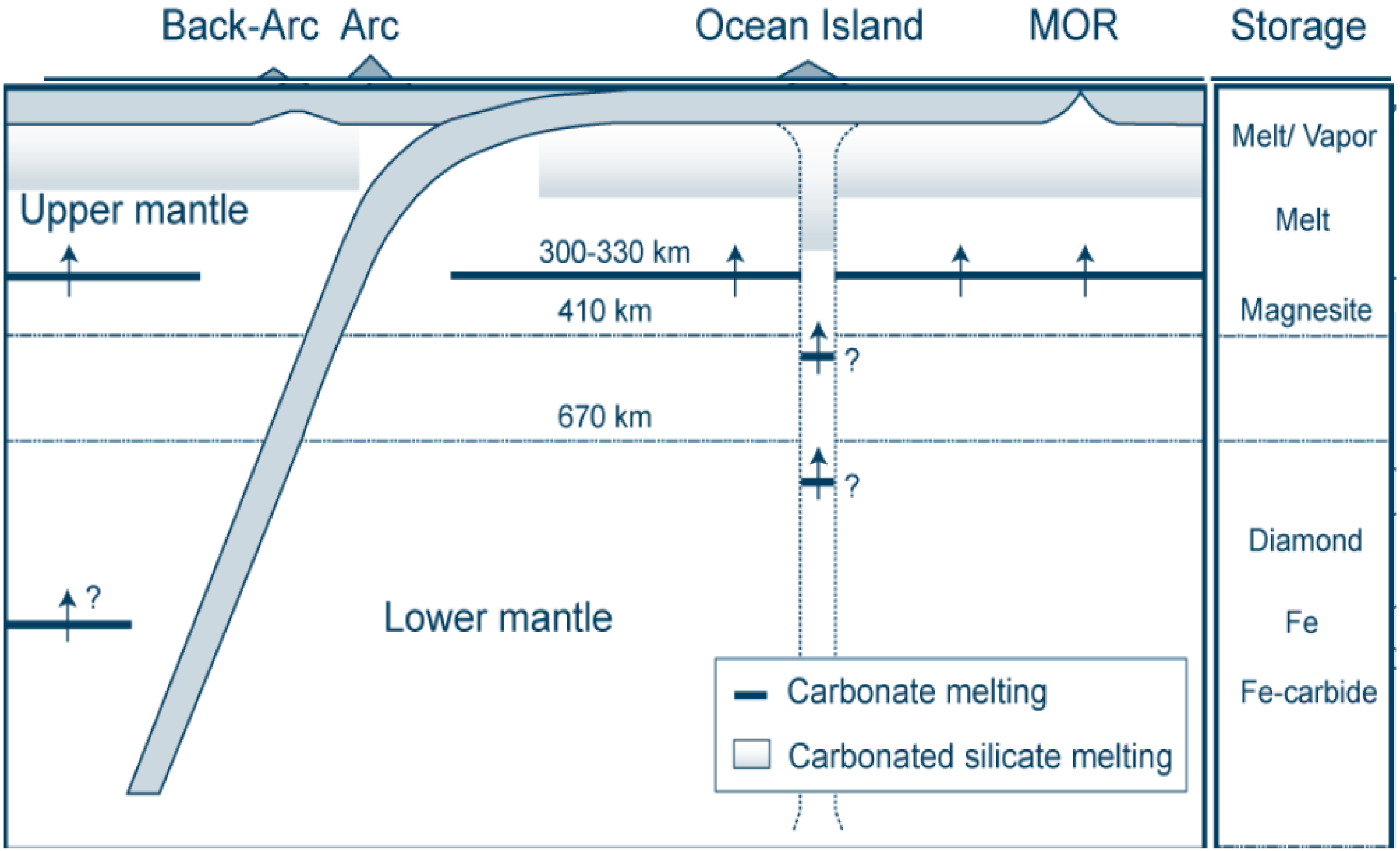
Deep Carbon cycling beneath western Mediterranean region

Volcanic degassing:

- 20 -30 Mt/yr
- Non-volcanic degassing:
- 15 – 30 Mt/yr

- Carbonate-rich melts 45% CO_2 by weight.
- 0.1 - 1 wt% of carbonate melt concentration, and 100% degassing=1.35 – 13.5 Mt of CO_2 (equal to 0.4 - 4 Mt carbon) for each km^3 of metasomatized mantle.
- Assuming 30 M.y., CO_2 degassing of the low velocity wedge beneath the Western Mediterranean would conservatively lead to lithosphere-asthenosphere CO_2 flux of about 60 - 600 Mt/yr

Deep Carbon cycling



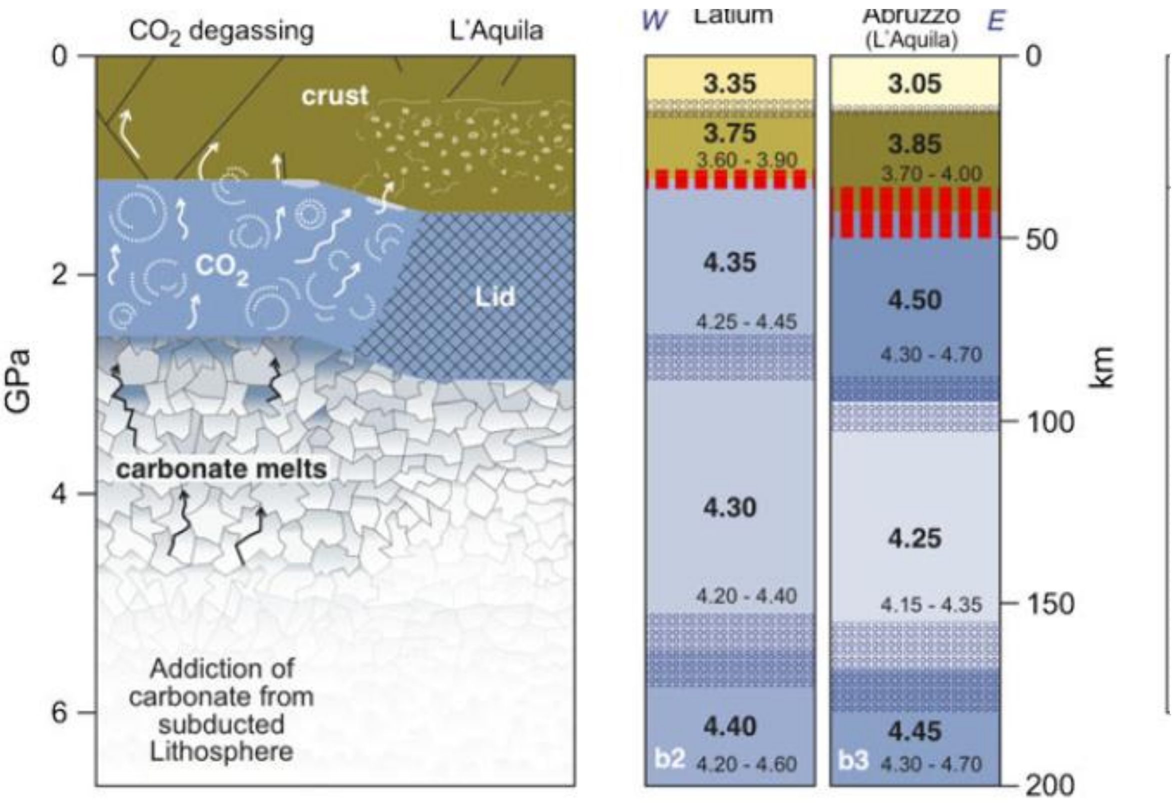
Dasgupta & Hirschmann, 2010 EPSL

Conclusions

The long-term fluxes in the carbon cycle control the Earth's long-term climate.

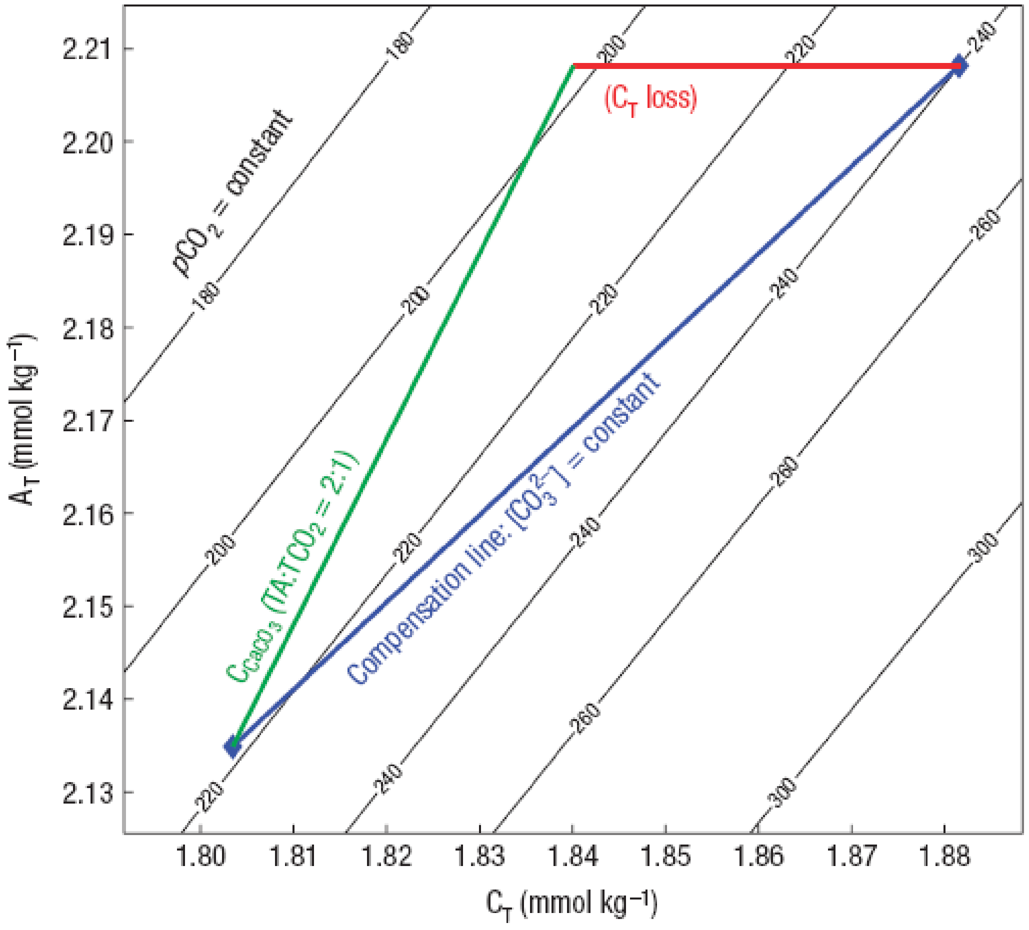
Petrological modelling of carbon cycling suggests that carbonated rock melting regulate the deep carbon fluxes from the mantle at the global scale

The introduction of other variables (e.g. fO_2) will improve modeling deep carbon cycling


CO2 degassing
L'Aquila
crust
CO2
Lid
carbonate melts
Addiction of carbonate from subducted Lithosphere
GPa
0
2
4
6
W
Latium
Abruzzo
(L'Aquila)
E
3.35
3.75
3.60 - 3.90
4.35
4.25 - 4.45
4.30
4.20 - 4.40
4.40
b2
4.20 - 4.60
3.05
3.85
3.70 - 4.00
4.50
4.30 - 4.70
4.25
4.15 - 4.35
4.45
b3
4.30 - 4.70
km
0
50
100
150
200

Imbalance of long-term Carbon fluxes

- Imbalance 1-2% past 610 kyr
- -22 to +10 ppm CO2 in atmosphere
- Carbonate compensation (10 kyr)



Zeebe and Caldeira, 2008 Nature G

- Camerino, 18 Gennaio (Dipartimento di Scienze della Terra);
  Urbino, 19 gennaio (Scuola di Dottorato in Scienze della Terra);
  Siena, 26 gennaio (Scuola di Dottorato in Scienze della Terra-Preistoria);
  Padova, 2 febbraio (Dipartimento di Geoscienze);
  Parma, 15 febbraio (Dipartimento di Scienze della Terra);
  Genova, 16 febbraio (Scuola di Dottorato STAT);
  Torino, 23 febbraio (Dipartimento di Scienze Mineralogiche e Petrologiche);
  San Marco in Lamis (FG), 1 marzo (Museo del Carsismo e dei Dinosauri).