

Introduction to the Thematic set: Carbon forms, paths and processes in the Earth



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Carbon forms: paths and processes in the Earth is a thematic set of six papers arising from the lectures presented at the Lake Como School, held at Villa del Grumello, Como, Italy (15–20 October 2017), and organized by the Graduate School of Milano Bicocca. This collection of lecture notes focusses on the structure of carbon allotropes, the geodynamics of deep Earth's carbon transport and fixation at mantle conditions, carbon degassing by ascending magmas, and the vast tectonic carbon degassing at the Earth's surface.

New science is emerging for carbon, one of the fundamental elements for life, energy, and global climate change on our planet. Carbon is cycled between surface, atmosphere, and oceans. Most of the recyclable carbon is stored deep in the Earth. Ingassing from the atmo-hydrosphere into the mantle occurs by subduction; in the mantle carbon resides in solids such as diamonds and is transported by fluids and melts that migrate upward. Outgassing into the atmosphere is effected by volcanism and tectono-metamorphic soil emissions. The forms and processes of carbon ingassing and outgassing are still poorly constrained. There is as yet no consensus on how and when carbon transforms from solid to fluid phases and vice versa, nor even on the processes that regulate carbon fluxes between Earth's reservoirs. These emerging research themes are crucial to gain insights in the past and present evolution of our planet and constitute building blocks to address current challenges of climate change. The six papers of the present thematic set focus on the forms, paths, and processes of Earth's carbon.

Langenhorst & Campione (2018) explore the fundamental physical and chemical properties of ideal and real solid carbon forms as a function of pressure and temperature (P-T), and describe the ideal structural models of fundamental carbon allotropes. They show how the properties of graphene and diamond molecules vary with crystallite size. Imperfections in crystal structures of natural carbon allotropes are interpreted as fingerprints of the geological environment in which they formed.

Sverjensky (2019) provides the quantitative thermodynamic basis needed to carry out theoretical geochemical modeling of fluids and fluid-rock interactions from the surface to upper mantle conditions. He describes the general criteria for predicting equilibrium and non-equilibrium reactions, followed by a summary of how the thermodynamic activities of species are related to measurable concentrations through standard states and activity coefficients. The concept of aqueous speciation, and the way to calculate it, arises from this discussion. His DEW (Deep Earth Water) model includes a revised Helgeson-Kirkham-Flowers equation of state and revised predictive correlations for the

estimation of equation of state coefficients. Finally, the DEW model is applied to the solubility and speciation of aqueous aluminium.

The third and fourth papers explore the nature of carbon reservoirs and carbon transport deep in the Earth's interior. Stagno (2019) reports the current state of research on naturally occurring deep carbon phases (e.g. diamond, carbides, carbonates, and carbonatitic melts) at mantle pressure and temperature conditions, carbon mobilization in the asthenospheric mantle by redox partial melting, and its sequestration during subduction by redox freezing processes. Through time, the redox state the Earth's mantle has strongly influenced the speciation of carbon from the mantle to mantle-derived magmas as well as from volcanic emissions. Tumiati & Malaspina (2018) illustrate how carbon can be a redox-controlling factor when it is transferred from the subducting plate to the mantle wedge. They explore fluid-mediated processes at the slab-mantle interface considering different fluid/rock ratios. Comparing thermodynamic modeling with experimental results, they show how carbon speciation in C-O-H fluids can affect the stability of hydrous and carbonate minerals, and the solidus of peridotites.

Transfer of deep carbon to the Earth's surface constitutes the theme of the fifth and sixth papers. Moore & Bodnar (2019) estimate the amount and distribution of CO₂ degassed by magmas, using as an example the Kilauea volcanic system (Hawaii). They calculate first-order estimates regarding: (i) the original concentration of CO₂ in magma generated by melting a carbon-bearing source, (ii) the successive enrichment of CO₂ in the melt during fractional crystallization, (iii) volatile saturation and exsolution of CO₂ from a fluid-saturated melt, and (iv) the outgassing from the volcanic edifice. Frondini *et al.* (2018) review fluxes to the atmosphere by diffuse degassing of deep carbon from tectonic structures, concentrating on the case of the Italian Apennines. They report on the methods used to measure the regional flux of deep CO₂ associated with groundwater circulation and comment on the relationships between the regional CO₂ flux and areas of focused and diffuse gas emission from soil. Further, they illustrate the relationships between regional CO₂ degassing and advective heat flow. Carbon balance of regional aquifers in the Apennine region shows that diffuse tectono-metamorphic CO₂ degassing is the major component of the geological contribution to the atmosphere in Italy, prevailing over the CO₂ degassed by active volcanoes.

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