THEME 3: Volatiles of the Earth

Session 3.5:

Volatile components in the deep Earth

CONVENED BY:
BJØRN MYSEN (B.MYSEN@GL.CIW.EDU)
MIKE CARROLL (MICHAEL.CARROLL@UNICAM.IT)
DAVID L. KOHLSTED (DLKOHL@UMN.EDU)

INVITED SPEAKERS:
SHUN –ICHIRO KARATO (SHUN-ICHIRO.KARATO@YALE.EDU)
CRAIG MANNING (MANNING@ESS.UCLA.EDU)
STEFANO POLI (STEFANO.POLI@UNIMI.IT)
KENJI MIBE (MIBE@ERI.U-TOKYO.AC.JP)
MAX SCHMIDT (MAX.SCHMIDT@ERDW.ETHZ.CH)

This session aims to trace the behaviour of volatiles as well as their influence on physical and chemical properties during their transfer from the surface to the deep Earth and back to the surface. The symposium will address PVT properties of volatiles in the C O H system as well as silicate solubility in C O H fluids at high pressure. It will also examine devolatilization equilibria in the pressure/temperature regime of subduction and the fate of volatiles bound in dense hydrous magnesium silicate minerals as well as nominally anhydrous minerals in the upper and lower mantle and the transition zone. The carbon cycle in the Earth's interior will be explored via carbonate stability relations and the CO_2 graphite diamond relations in the deep upper mantle and below. The rheological and transport properties of dry and wet mantle minerals at high pressures will be discussed. This session will also focus on transport of volatiles as a free phase ("wetting angle restrictions") as a function of pressure, temperature, and silicate compositions, the fluxing effects of C O H volatiles on melting behaviour in the interior of the Earth, solubility and solubility mechanisms of C-O-H volatiles in silicate melts and minerals, relationships between volatile content of silicate melts and minerals and their physical and chemical properties in the Earth's interior.

3.5.11

Generation of C-O-H fluids from subducted altered oceanic crust: An experimental perspective

A. CROTTINI AND S. POLI

Università di Milano, Dipartimento di Scienze della Terra (Ada.Crottini@unimi.it; Stefano.Poli@unimi.it)

Phase relationships among hydrates, carbonates and graphite/diamond in subduction environments are responsible for volatile transfer from the slab to the mantle wedge. Despite the relevance of such coexisting phases for the global geochemical cycle of C-O-H species, their mutual stabilities as a function of P, T and oxygen or hydrogen fugacity are still poorly explored.

Experiments were carried out using piston-cylinder and multianvil machines at pressures from 1 to 5 GPa and temperatures from 650 °C to 800 °C. Seeded gels were used as starting materials in a model MORB system, in the presence of a fluid at variable C-O-H ratios generated from three mixtures of oxalic acid dihydrate and silver oxalate. The double capsule technique was employed to control fH_2 at Ni-NiO (NNO, OH) and hematite-magnetite (HM, OH) buffers (notation after [1]). Run products were characterized by XRPD, SEM, WDS-EMPA, and Raman spectroscopy.

At NNO hydrogen fugacities, a large amphibole-carbonate phase field is present up to $P < 2$ GPa in H_2O rich compositions. Amphibole breaks down at 2.5-2.6 GPa, epidote persists to 2.7 GPa, 730°C and talc to 3.3 GPa 800 °C. Graphite is ubiquitous above 1.8 GPa. Dolomite and magnesite are stable between 1.6 and 2.0 GPa, but disappear at higher pressures, being graphite the only C-bearing solid phase. Thermodynamic and mass-balance estimates of coexisting C-O-H fluids at fO_2 NNO, OH (XG, COH) suggest equilibrium with H_2O-rich fluids.

Conversely, at HM buffer (which implies oxygen fugacities close to GCO buffer in the inner charge), carbonate phase fields get wider with pressure: aragonite and/or dolomite are stable up to 2.4 GPa and at higher pressure they are replaced by magnesite and dolomite. Mg-calcite was found at 5 GPa 800 °C. Coexisting fluids are graphite-saturated and CO_2 enriched.

As a result of complex mass-balance relations which describe the partitioning of volatiles between fluid and solid phases at fixed hydrogen fugacities, carbonate stabilities are strongly influenced by the amount of C-O-H components in the charge. On the other hand, in natural rocks, with increasing pressure, hydrate-carbonate-graphite/diamond equilibria are expected to "buffer" fluid speciation at high oxygen fugacities and relatively CO_2-rich compositions.

References

[1] Eugster H.P. and Skippen G.B. (1967) *Researches in Geochemistry* **2,** 492-526