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► **To cite this version:**

Michel Pichavant, Bruno Scaillet, Caroline Martel. Experimental Phase Equilibria: Data and Models. ESF LESC exploratory workshop on “ Gases in magmatic evolution : from depth to atmosphere, from micro to macro-sacle, from calculation to observation ”, 2003, Rome, Italy. pp.44-45. hal-00102666

HAL Id: hal-00102666

<https://hal-insu.archives-ouvertes.fr/hal-00102666>

Submitted on 2 Oct 2006

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Experimental Phase Equilibria: Data and Models

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Equilibria between silicate melts, crystalline and vapour phases essentially control major and trace element compositions of natural magmas and play an essential role in partial melting as well as in differentiation processes. The development of models of phase equilibria is a prerequisite for assessing the dynamics of magmatic processes, such as magma storage in a reservoir or magma ascent in a conduit. The interest of experimental phase equilibria is essentially twofold. (1) Experimental phase equilibrium results can put precise constraints on the magmatic conditions, either in the magma storage region or in the conduit. Knowledge of pre-eruptive parameters (P, T, H₂O in melt, fO₂, ...) is necessary for eruption models and consequently for the evaluation of volcanic risk. (2) Experimental phase equilibria constitute our main source of information for the calibration of the mixing properties of multicomponent silicate melts, and for the construction of thermodynamic models which are our tomorrow's tools for the simulation of magmatic processes. This presentation will review recent developments and trends in the field of experimental phase equilibria on natural magmas. Areas where future research is needed will be identified. During the last 20 years, experimental phase equilibria have been increasingly used for the determination of the pre-eruptive conditions of subvolcanic magma bodies, essentially from convergent plate boundaries because of the high level of associated volcanic risk. Following technical (eg, control of redox conditions) and analytical (eg, H₂O determination) developments during that period, natural magmatic conditions can now be precisely controlled in the laboratory. Conditions of phenocryst growth and equilibration can be determined by comparison with natural phase assemblages and compositions. In comparison with the petrologic approach (mineral-mineral or mineral-melt thermobarometry, glass inclusions), the experimental approach generally offers greater sensitivity and accuracy on key pre-eruptive parameters such as melt H₂O content and pressure of magma storage. The experimental approach has been applied mostly to silicic magmas, ranging from andesitic to rhyolitic [Mt. St. Helens, Rutherford et al., 1985; Mt. Pelée, Martel et al., 1998; 1999; Mt. Pinatubo, Scaillet and Evans, 1999] and at relatively low pressures

(< 4 kbar) corresponding to the depth (< 15 km) of subvolcanic magma reservoirs. Conditions of magma storage have been determined for a number of active silicic volcanoes and this has allowed to place tight constraints on volatile abundance in arc magmas and on the composition of the magmatic vapour phase [Scaillet and Pichavant, 2003]. In comparison, only a very limited number of studies has been carried out on basaltic compositions. Several European volcanoes erupt primitive basaltic compositions and there is a need for future studies on such compositions in presence of volatiles (H₂O, CO₂, S). There is also a need for performing such experiments at pressures (4-10 kbar) appropriate for the differentiation of basaltic magmas in the crust.

More recently, phase equilibrium experiments have been extended to simulate conditions and processes that take place in the conduit during an eruption, such as degassing and microlite crystallization [Martel and Schmidt, 2002]. It is worth pointing out that most experiments in this category are not of the equilibrium type (most are decompression experiments in which pressure is allowed to vary within certain bounds and at certain rates). However, the results are analyzed in the light of equilibrium experiments performed in parallel at different pressures, with the aim to provide information on the degree of disequilibrium, on the kinetics of crystallization and, ultimately on the timescales of events occurring in the conduit.

The available thermodynamic models for multicomponent melts are still imperfectly calibrated and far to cover the range of natural compositions and mineral-melt equilibria. The construction of such models requires an integrated effort from different approaches. Standard state properties and volumes must be known (and continuously refined) for more than 10 components. The determination of experimental data such as phase equilibria (and activity measurements) should be pursued in critical parts of the compositional space to improve the calibration of G_{mix} for multicomponent melts. In parallel, more data are necessary on the crystalchemistry, thermochemical data and mixing properties of several groups of minerals (micas, amphiboles) that need to be included in priority in the models. Software models such as MELTS [Ghiorso and Sack, 1995] or COMAGMAT [Ariskin et al., 1993] perform rather well for anhydrous low-pressure mafic melts. Their extension to hydrous compositions requires an experimental effort on phase equilibria in volatile-bearing basaltic melt compositions. Conversely, models exist for hydrous haplogranitic compositions [Kirschen and Pichavant, 2001]. However, to be applicable

to natural magmas, components such as CaO and FeO/Fe₂O₃ need to be included in priority. Phases such as micas and amphiboles must be included and the different phase equilibrium studies performed during the last few years on andesitic to rhyolitic compositions should be used in the calibration.

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