

## Effect of pressure on oxygen fugacities in magma oceans

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Oxygen fugacities in a magma ocean (MO) may have a crucial influence on removal of siderophile and volatile elements to the core during metal-silicate interaction and may control the composition and redox state of the overlying primitive atmosphere. However, the  $f_{O_2}$  prevailing at depth where metal equilibrates with silicate could be quite variable and remains controversial. Importantly, the  $f_{O_2}$  at the MO surface may not be similar to that at depth, owing to the effect of pressure on the chemical potentials of redox-sensitive elements, most notably iron.

Iron is the most abundant multi-valent element in silicate melts and so magmatic  $Fe^{3+}/\Sigma Fe$  ratios are linked directly to MO  $f_{O_2}$ . In a vigorously convecting, well-mixed MO, the variation with depth in the  $f_{O_2}$  may be set by a uniform  $Fe^{3+}/\Sigma Fe$  ratio of the silicate liquid, which in turn is fixed by magma-metal equilibration at high pressure. To determine this effect, one must know how magmatic  $Fe^{3+}/\Sigma Fe$  varies with pressure at known  $f_{O_2}$  and temperature. Experiments on an andesitic liquid up to 7 GPa and 1750°C, analyzed by Mossbauer spectroscopy, show that  $Fe^{3+}/\Sigma Fe$  ratios decrease with increasing pressure and temperature. If this trend continues at higher pressure, it suggests a MO with fixed  $Fe^{3+}/\Sigma Fe$  is more reduced in its shallow portions than it is at depth. However, considering the different compressibilities of  $Fe^{2+}$  and  $Fe^{3+}$  in silicate liquid, the trend may reverse at higher pressure and experiments above 7 GPa are in progress.

It is clear that the oxidation state of atmospheres overlying MOs may be related to the depth at which equilibrium is established between Fe-rich alloy and silicate, with consequences for evolution of early atmospheres and climate, and the origin of life. If shallow MOs are related to reducing atmospheres and deep high pressure ones related to oxidizing atmospheres, then smaller planets that equilibrate with iron at low pressure may yield early atmospheres rich in CO and H<sub>2</sub>. Larger ones equilibrating with Fe at higher pressure, may yield early atmospheres rich in CO<sub>2</sub> and H<sub>2</sub>O.

## Elasticity and structure of mantle pyroxenes

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To understand complex upper mantle seismic structure we must know the single-crystal elastic properties of the constituent minerals at high pressures and temperatures. Here we report recent work on the single-crystal elastic properties and phase transitions in Ca-poor orthopyroxene and Ca-rich clinopyroxene at high pressures. The elastic properties of natural orthoenstatite (OEN) and natural diopside have been determined at high pressures to over 14 GPa at room temperature by Brillouin spectroscopy. Single crystals of Fe-bearing orthoenstatite from San Carlos were used in the study. Sound velocity data display a pronounced change upon cold compression to above 12 GPa, and an abrupt change in velocity anisotropy. Single-crystal X-ray structure refinements show that OEN transforms to a new high-pressure phase with space group P21/c, with the transition pressure bracketed between about 10-14 GPa. No evidence of a C2/c structure was observed. Raman spectroscopy on nearly pure Mg OPX, a high-alumina sample, and an Fe-rich sample show that Al and Fe both effect the transition pressure, but that the high-pressure phase is still P21/c in all cases.

The single-crystal elasticity diopside was measured to transition zone pressures using Brillouin spectroscopy. It shows a markedly different behaviour to that of OEN. The  $C_{ij}$ 's as a function of pressure were obtained. Aggregate bulk elastic properties are in very good agreement with polycrystalline acoustic measurements. In the case of diopside single-crystal Brillouin and polycrystalline acoustic measurements give highly consistent results.