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HP *ab-initio* study of dolomite compressibility as influenced by cation disordering.

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Dolomite [$CaMg(CO_3)_2$] is the most abundant double carbonate in nature. A fully ordered dolomite consists of alternated calcium and magnesium layers separated by carbonate groups (CO_3^{2-}); disordered cationic configurations can arise as Ca and Mg randomly distribute over dolomite crystallographic sites. The stability field of dolomite extends from sedimentary up to high temperature (HT) - high pressure (HP) conditions being the mineral stable at mantle conditions down to approximately 250 km depending on the rate of subduction as well as on the crystallographic characteristics of the mineral, *i.e.* the dolomite stability field is contracted as cation disorder arises in the dolomite structure [1]. However, experiments at HP conditions on the compressional behavior of disordered dolomite have not been performed since the non-quenchability of disordered crystal structures [2][3]. Therefore, an *ab initio* study was carried out in order to analyze the baric behavior of differently ordered dolomite structures.

Two configurations were used, a fully-ordered dolomite (SC1) and a partially-disordered one (SC4895) characterized by an order parameter s[2] = 0.5, as these have been account as the most probable configurations at lower and higher T respectively [4]. Total static energy calculations were performed at the hybrid Hartree-Fock/Density-Functional-Theory level by means of CRYSTAL09 code [5]. Volume cell variations and energy minimization at each optimized geometry were performed. The corresponding P range was approximately 0-13 GPa.

Mean linear compressibility of **a** and **c** axes shows a strong anisotropy (**c/a** compressibility ratio is approximately 3:1). $P - V$ data were fitted by a third order Birch-Murnaghan Equation of State and results were K_0 = 93.4 GPa (K_0' = 4.7) for the ordered configurations and K_0 = 92.3 GPa (K_0' = 4.4) for the disordered one. They become K_0 = 95.9 GPa and K_0 = 93.9 GPa respectively, when K_0' is fixed to 4.

Notwithstanding SC4895 is not a completely-disordered configuration due to computational issues [4], it has a lower bulk modulus with respect to the ordered phase. Thus, cation disordering seems to act in slightly increasing volume compressibility of dolomite.

Our previous studies [4] have shown that an intra-layer type disordering is the most probable driving mechanism for cation distribution in dolomite as T increases. Therefore, we can hereby speculate that the thermal structure of subduction zones, affecting the order/disorder conditions of dolomite, plays a fundamental rule on the compressional behavior of the mineral during the subduction. This should influence the decarbonation conditions and, in turn, the release of *carbon* from the slab to the mantle wedge at subduction zones.

[1] Hammouda et al. (2011) *Contrib. Mineral. Petrol.*, **161**, 439-450; [2] Reeder & Wenk (1983) *Am. Mineral.*, **68**, 769-776; [3] Zucchini et al. (2012) *Phys. Chem. Minerals*, **39**, 319-328; [4] Zucchini et al., submitted to *Calphad*; [5] Dovesi et al. (2009) CRYSTAL09 (CRYSTAL09 User's Manual. University of Turin, Turin).