Dolomite discloses a hidden history of subducting slabs

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Abstract: Dolomite and magnesite are the major carbon reservoirs in the subducted oceanic lithosphere. Compositional complexities in dolomite and magnesite solid solutions are often overlooked, but normal and oscillatory zoning in dolomite from mafic eclogites of Tianshan (China) demonstrates that prograde pressure – temperature histories and interactions with coexisting mixed fluids can be recorded in carbonates. Thermodynamic modelling and comparison with experimental results warn against a simplistic approach to carbonate-bearing assemblages and show that magnesite occurrence is not an unambiguous evidence for ultra-high pressure metamorphism.

Keywords: dolomite, magnesite, eclogite, Tianshan, oscillatory zoning, REE

The last decade has witnessed an increasing effort on the part of Earth scientists to decipher the fate of carbon at convergent margins, and how such fate relates to redox processes through time (Hayes and Waldbauer 2006). Carbonates are major constituents of the altered oceanic crust and of the sedimentary materials entering the orogenic cycle. Extensive experimental work on phase relationships in carbon-bearing systems reveals that carbonates are extremely stable at mantle pressures and the transfer of carbon to the mantle wedge at subduction zones is linked to the extent of decarbonation and/or dissolution in aqueous fluids, or to the attainment of a carbonatitic solidus if a thermal relaxation occurs, e.g. upon subduction stagnation.

Despite the variety of scenarios invoked in the literature to explain the transfer of carbon from the subducted slab to the subarc mantle and to constrain the source of CO_2 species in magmatic arcs, little is known of the natural record of carbonate-bearing assemblages in eclogites and related rocks.

Most current knowledge of phase relationships in carbonate-bearing rocks that experienced high or ultra-high pressure conditions derives from just a few localities and mostly from marbles, i.e. at Kokchetav massif, Kazakhstan (Korsakov and Hermann 2006); Tianshan and Dabie-SuLu, China (Lu et al. 2013, Proyer et al. 2013); Zermatt-Saas and Dora-Maira, Western Alps (Reinecke 1998, Castelli et al. 2007). Experimental studies provide an extended frame, though not exhaustive, of mineral assemblages in model chemical systems at high pressures (Poli et al. 2009, Grassi and Schmidt 2011, Dasgupta et al. 2004, Tumiati et al. 2013); however, the reconstruction of the prograde temperature evolution as recorded by carbonated eclogites is hindered by difficulties in identifying unequivocal remnants of the earliest stages of subduction history.

Although expected to be common at high-pressure, compositional complexities in dolomite and magnesite solid solutions are overlooked, because carbonates are often regarded as being very reactive upon retrograde processes and because thermodynamic modelling of ternary Ca-Mg-Fe carbonates has been only recently re-assessed. Li et al. (2014) provide an excellent example of such compositional variations both in dolomite and magnesite in a mafic eclogite sample from SW Tianshan, China. Notably, dolomite displays spectacular zoning organized in both normal and oscillatory patterns. Li et al provide an unprecedented documentation for metamorphic rocks that shows how carbonates are able to record a long history in the pressure-temperature evolution during subduction. Unexpectedly, similarly to garnet, dolomite crystal chemistry provides a robust indication of a prograde path, moving from calcite/aragonite- to magnesite-bearing mineral assemblages at more than 600 °C at 2.3 GPa. Thermodynamic modelling performed by the authors testifies to the continuous transformations from the blueschist assemblage aragonite + chlorite + glaucophane + lawsonite up to the eclogite facies peak conditions where dolomite + magnesite + omphacite + garnet + epidote coexist. Along this path, the Mg/(Mg+Fe) ratio in dolomite was found to increase from 0.65 to 0.80 and trace element content (e.g. REE) decreases by almost two orders of magnitude.

Detailed growth features of dolomite and preservation of older crystallization events can be understood on the basis of recent experimental results by Davis et al (2001) which show that the grain growth constant for dolomite is three orders of magnitude lower than that of calcite and more than one order lower than that of magnesite; zonation should be therefore the rule rather than the exception. Dolomite and, secondarily, magnesite are potential coffers of information still little explored in metamorphic petrology.

One of the most fascinating discoveries in this sample from Tianshan is the occurrence of delicate oscillatory zoning in the rim of dolomite, recorded by variations in Fe, Mg, Mn, but also possibly (see Fig. 5 in Li et al., this volume) REE , Y, Li; on the contrary other trace elements, e.g. Pb or Sr do not show similar variations. Oscillations are consistent with the occurrence of a fluid possibly generated by the prograde reactions consuming both amphibole and lawsonite. Differences in the behaviour of major and trace elements fluctuating in dolomite reveal different solubility and therefore a key for understanding element mobility in COH mixed fluids. Whether chemical variations should be related to intrinsic or extrinsic mechanisms (Shore and Fowler 1996) is a guiding question for future research.

Fluid release from the subducting slab is one of the pre-requisites for mantle metasomatism, i.e. for volatile and LILE addition to wedge peridotites triggering magma genesis. Carbonates are known to be soluble in aqueous fluids and they are therefore suitable trace element reservoirs amenable for transferring their load to migrating fluids. Trace element pattern in dolomite from mafic eclogites in Tianshan reveals a progressive increase in element content from La to Eu and a less pronounced decrease from Gd to Lu. On the contrary magnesite displays a continuous increase from LREE to HREE. To my knowledge, the only data available on dolomite from mafic eclogites were reported in a study on Dabie Sulu (Sassi et al 2000), but REE patterns are flat, approximately chondritic. There is no additional information on magnesite trace element content for mafic eclogites. Li et al (2014) therefore provide here a first look at trace element complexities in coexisting carbonates formed at high pressure, enlightening how poor current knowledge on this mineral group still is.

One additional important conclusion of the results of Li et al (2014) is that magnesite does not present unambiguous evidence for ultra-high pressure metamorphism. Consistent with experimental studies performed in mafic eclogites, magnesite is found to coexist with dolomite at pressures in the order of 2 GPa, forming at the expense of glaucophane. The complexity in thermodynamics of Ca-Mg-Fe carbonates warns against a simplistic interpretation based on Fe-free model systems. Dolomite is a very common rock-forming mineral still waiting for further exploration and for innovative applications to the reconstruction of dynamic processes in the Earth's interior.

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