Isotopic and petrologic evidence for graphite formation by carbonate reduction in blueschist metamorphic rocks

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The formation of carbonaceous material by abiotic processes is an important standing issue. This process depends on redox conditions and fluid/rock interactions. Subduction zones are major interfaces between the surficial and the deep Earth carbon reservoirs where complex processes affecting carbon transfers are still poorly known.

Here, we studied the geochemistry of carbon (reduced and oxidized) in siliceous-marbles at the direct contact with serpentinites in the Alpine eclogitic meta-ophiolithic units of northern Corsica (France). We applied spectroscopic (Raman) and isotopic techniques to characterize the carbonaceous and carbonate reservoirs in the rocks across a reaction front where the reaction $CaCO_3+SiO_2+2H_2=CaSiO_3+C+2H_2O$ is evidenced.

The reaction zone consists in a centimeter-thick pale nephrite layer lying at the contact with serpentinites, overlaid by a thin wollastonite layer and a 5 to 20 cm thick dark zone composed of wollastonite, carbonaceous material (CM) and quartz. No carbonate could be evidenced in that reaction zone. There is a sharp (<0.5cm) transition between this reaction zone and the overlying "primary" metasediment, which is composed of calcite+quartz and contains significantly less CM. Raman spectroscopy shows that CM is much more graphitic in the reaction zone than in the "primary" metasediment. Significant isotopic differences are observed between the reaction zone and the overlying "primary" metasediment: $\delta^{13}C$ values are around -15‰ and 1.3‰ for CM and calcite respectively in the "primary" metasediment far from the reaction zone, whereas $\delta^{13}C$ (CM) is around -1‰ in the reaction zone.

We interpret the graphitic CM in the reaction zone as formed by the destabilization and reduction of calcite subsequently to the diffusion of reducing fluids from the underlying serpentinite unit. Mass balance calculations support this hypothesis and shows that a complete reduction of carbonates may have occurred. The timing of the formation of this abiotic macromolecular and graphitic C, and the possible role of catalysts is discussed. The geological importance of this process in the subduction zone carbon cycling will be critically assessed.

Constraints on the Mg initial isotopic composition of the solar system from CM & CR chondrite

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The recent evaluation of the Al-Mg systematic in undifferentiated and differentiated meteorites at high precision using MC-SIMS or MC-ICPMS has returned conflicting information about the heterogeneity in the initial abundance of short-lived ^{26}Al (half-life of 0.73Ma) and in the Mg isotopic composition of the solar nebula (SN) [1-4]. Heterogeneity in the initial abundance of ^{26}Mg ($\delta^{26}Mg^{*}_{0}$) would prevent the use of olivine for dating the last thermal event [4] while $^{26}Al/^{27}Al$ heterogeneity would preclude any dating with Al-Mg.

Here, we report data, on the DSM3 scale, for Tafassasset, an equilibrated CR chondrite and for Paris, a well preserved CM chondrite. Sequential dissolution steps of bulk rock powder were performed but also separated minerals of olivine (Forsterite and Fayalite?) in Paris, accessory chromite (Tafassasset) and an aliquot of the bulk rock were analyzed for Al/Mg systematic. These fractions correspond to aliquots from the detailed Mn/Cr systematic study that suggested an age of 4.8±0.4 and 7.8±0.6 Ma older than the angrite LEW Cliff 86010 for the CR and the CM, respectively [5]. In Tafassasset, the Mg isotopic composition is homogeneous with $\delta^{26}Mg$= - 0.30±0.05‰ and $\delta^{26}Mg^{*}$= - 0.002±0.015‰ ($2\sigma_{mean}$, N=5) except for the chromite with a $\delta^{26}Mg$= 0.24±0.07‰ and a $\delta^{26}Mg^{*}_{Bulk\ CR}$<0.038‰ at 95% confidence level. This would suggest a $^{26}Al/^{27}Al \leq 2\times10^{-6}$ at the time of the thermal equilibration of the chromite with the rest of the chondrite. The difference in the $\delta^{26}Mg$ suggests an Mg equilibrium temperature of 1180-1450ºK [6]. Assuming a homogeneous and initial $^{26}Al/^{27}Al$ of 5.23×10^{-5} for the SN, a $^{26}Al/^{27}Al \leq 2\times10^{-6}$ would only be compatible with the Mn-Cr age if the difference in age was > 9.5Ma between LEW Cliff 86010 and CAIs. Such an old age for the CAIs is also required from Hf-W systematic [7] and the chronological agreement between CAIs, CR and LEW Cliff 86010 for Al-Mg, Mn-Cr and Hf-W would support a homogeneous SN with respect to ^{26}Al [1-2]. In that case, the measured value implies $\delta^{26}Mg^{*}_{0}$= - 0.040±0.015‰ assuming a chondritic Al/Mg ratio for this CR. In Paris, the olivine fractions returned different Mg isotopic compositions. Their $\delta^{26}Mg^{*}$ are different by 0.064‰ just outside the $2\sigma_{mean}$. Given the old Mn/Cr age of this CM chondrite, the $\delta^{26}Mg^{*}_{0}$ is estimated to be - 0.006±0.039‰ ($2\sigma_{mean}$, for 4 objects defining the Mn-Cr isochron [5]). Altogether these data are more suggestive of small (~0.05‰) heterogeneity in the initial abundance of ^{26}Mg than of ^{26}Al in the SN. Attempt of detailed Al-Mg will be discussed but the small measured range of $\delta^{26}Mg^{*}$ (<0.15‰ at 95% confidence) is likely to prevent accurate determination of the $^{26}Al/^{27}Al$ for this CM.

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