THE COMPOSITIONAL VARIABILITY OF DOLOMITES IN CI CHONDRITES: IMPLICATIONS FOR PHYSICO-CHEMICAL CONDITIONS OF CIRCULATING FLUIDS ON THE CI PARENT BODY.
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Carbonate minerals are well known from carbonaceous chondrites which have experienced severe aqueous alteration. Especially CI chondrites contain a variety of carbonates, mainly dolomite and less abundant calcite and magnesite (breunnerite) [1-3]. These minerals are believed to have precipitated from aqueous solutions circulating on the CI parent body. Therefore, the understanding of carbonate formation is an important key in order to unravel the physico-chemical conditions of these solutions during the alteration event. For this study we determined the chemical composition of more than 150 dolomites in the CI chondrites Orgueil, Ivuna, and Alais by electron microprobe technique. In contrast to previous studies [1-4] we observed not only significant compositional differences between dolomites within one CI chondrite (as reported earlier [5]), but also differences between dolomites among CI chondrites. As a main result of this investigation we will demonstrate that the compositional variability of dolomites between different CIs is not controlled by variations of the Mn$^{2+}$ concentration (as it is the case for compositional differences between dolomites within one CI). Rather, the variability is due to variable temperatures and/or pH-, Eh-, and pCO$_2$-conditions in the fluids.

Results: Dolomites occur in all studied CI chondrites and are usually <10 to ~300 μm in size (mm-sized dolomites have been reported by [3]). The 100-300 μm size range is restricted to carbonate fragments, which apparently are remnants of former carbonate veins [5]. The distribution of dolomites in each CI chondrite is very heterogeneous. Some matrix clasts contain up to 10 vol% dolomites [5], in others they are almost lacking. CI dolomites are predominantly manganese-bearing dolomites (up to 15 wt% MnO), carrying small amounts of Fe as well. The overall compositional variability of dolomites in terms of their CaCO$_3$, MgCO$_3$, MnCO$_3$ and FeCO$_3$-contents can be expressed as $(\text{Ca},0.35-0.33,\text{Mg},0.34-0.31,\text{Mn},0.00-0.15,\text{Fe},0.02-0.13)\text{CO}_3$, which is in good agreement with results of most previous studies [2,3]. Important differences between dolomites in Orgueil, Ivuna, and Alais become obvious from Fig.1, where different dolomite components are plotted against each other. Two general results can be conducted. First, compared to dolomites from Orgueil and Ivuna dolomites from Alais show a very narrow range of Ca/Mg-ratios. Second, as already reported earlier [3,4] most CI dolomites show significant deviations from the ideal Ca:Mg=1:1 stoichiometry, due to the incorporation of Mn$^{2+}$ onto the Ca$^{2+}$ lattice sites of the dolomite structure.

Additionally, important characteristics of dolomites in Orgueil, Ivuna, and Alais are apparent from Fig.1, which can be summarized as follows:

(1) Ivuna: Dolomites show slightly negative correlations between the MgCO$_3$- and MnCO$_3$-contents and the CaCO$_3$- and MnCO$_3$-contents. The CaCO$_3$- and MgCO$_3$-contents are decoupled.

(2) Orgueil: A negative correlation between the MgCO$_3$- and MnCO$_3$-contents of dolomites exists. The CaCO$_3$- and MgCO$_3$-contents are coupled (negative correlation).

(3) Alais: Dolomites exhibit a negative correlation between (a) the MgCO$_3$- and MnCO$_3$-contents, (b) the MgCO$_3$- and FeCO$_3$-contents, and (c) the CaCO$_3$- and MnCO$_3$-contents. The CaCO$_3$- and MgCO$_3$-contents are coupled (positive correlation). Alais contains two different dolomite generations, which can be separated by their MnCO$_3$-contents.

Discussion: The mentioned dolomite characteristics cannot be explained by simple variations of the Mn$^{2+}$ concentration in the circulating fluids on the CI parent body. Rather, we suggest that the correlations between different components in dolomites from Orgueil, Ivuna, and Alais reflect the structural behavior of Mn$^{2+}$ ions in different physico-chemical settings (e.g. different temperature and Eh-, pH-, pCO$_2$-values) during carbonate precipitation. The importance of such parameters for carbonate formation is well known from experimental studies of terrestrial samples [6]. In Ivuna Mn$^{2+}$ ions are occupying both Ca$^{2+}$ and Mg$^{2+}$ cation sites in the dolomite structure. In contrast, in Orgueil dolomites Mn$^{2+}$ ions fill predominantly Mg$^{2+}$ lattice sites. However, in both Ivuna and Orgueil, the final composition of dolomites is linked to the Mn$^{2+}$ concentration in the aqueous solutions, confirming the results of [3,4]. This is not the case for dolomites in Alais. Like in Orgueil, Mn$^{2+}$ ions are capable of occupying Mg$^{2+}$ and Ca$^{2+}$ cation sites in the dolomite structure. Additionally, Fe$^{2+}$ ions partly fill Mg$^{2+}$ lattice sites. Therefore, the final composition of Alais dolomites depends on the Mn$^{2+}$ and Fe$^{2+}$ ion concentration in the fluids. The occurrence of two distinct dolomite generations in Alais puts further constraints on the formation history of carbonates in CIs. Since Alais is nearly unbrecciated (at least on a mm-scale) impact-induced mixing processes fail to account for the close neighbourhood of chemically different dolomites. Therefore, the two dolomite generations in Alais can only be explained by different formation ages. We can further assume that the physico-
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domestic settings during dolomite precipitation in Alais must have been similar for both generations, since otherwise the earlier generation would have been dissolved.

Conclusions: Different dolomite compositions within individual CI chondrites (like the compositional differences between dolomites in distinct lithic units in Ivuna as reported by [5]), are mainly due to the local (mm-scale) availability of Mg$^{2+}$, Ca$^{2+}$, Fe$^{2+}$, and especially Mn$^{2+}$ ions in the circulating fluids. Different dolomite compositions between different CI chondrites are probably reflecting global (km-scale (?)) differences in the physico-chemical conditions (e.g. temperatures and Eh-, pH-, pCO$_2$-values) of aqueous solutions on the CI parent body.


Fig. 1: Correlations between different components of dolomites in the CI chondrites Orgueil, Ivuna, and Alais.