

Geochemistry and Nd-Sr Isotopic Composition of Carbonate Rocks and Their Insoluble Materials: Implications for the Origin of Carbonate Rocks and the Average Chemical Composition of the Upper Continental Crust

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The genesis of dolomite in the natural environment remains one of the outstanding geological enigmas, despite of over two centuries of intensive research and debate. In this research we are concerned with the origin and weathering processes of carbonate rocks, and evaluation of the reconstruction of the chemical composition of the upper-continental crust through studies of the geochemistry of insoluble-residue materials in carbonate rocks. The samples analysed were collected from eight weathering profiles of carbonate rocks, ranging from Cambrian to Triassic in age, distributed in karst terrain of central and northern Guizhou Province. The experimental method for extracting insoluble-residue materials in carbonate rocks is the same as what is reported recently[1]. Mineral assemblages of insoluble-residue materials in carbonate rocks are quartz, illite, kaolinite and potassium for Cambrian dolostone, and quartz, illite, kaolinite, montmorillonite, feldspar (potassium, plagioclase), brookite and pyrite for Triassic carbonate rocks, but no plagioclase is recognized in the Triassic limestone and its main minerals are quartz and potassium that differ from the Triassic dolostone (clay minerals). The contents of insoluble-residue materials in carbonate rocks are highest in the Triassic limestone, and lowest in the Triassic dolostone. From the relations between $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios and CIA values (chemical index of alteration), the insoluble-residue materials in carbonate rocks must have subjected to moderate to intense chemical weathering. UCC-normalized trace element spidergrams of carbonate rocks and insoluble-residue materials are remarkably uniform, respectively, with the latter being strongly enriched in Mo and depleted in Sr, and the elements Th, Ta, Nb, Zr, Hf, etc. are least variable. The Sr, Fe, and Mn concentrations for the Triassic limestone are 371-796, 622-933 and 154 ppm, and for the Cambrian and Triassic dolostone are 61-134, 389-777 and 23-77 ppm, respectively. The good relationships between Al_2O_3 and high field strength element (TiO_2 , Nb, Zr), and between Nb/Ta, Zr/Hf, Rb/Cs element pairs of carbonate rocks and insoluble-residue materials are observed. Nb and Ta define a fairly constant ratio in all research samples (14.04), it is almost similar to that obtained by Plank and Langmuir (1998)[2] from subducting sediment. The REE patterns Triassic limestone are like to those of shales, and the others mostly close to those to seawater. Only one Triassic dolostone is characterized by large negative Ce anomalies with MREE and HREE enrichment, and its REE patterns are similar to the bell-shaped REE patterns of pre-Jurassic phosphate debris as described by Reynard et al. (1999)[3]. The REE patterns of

insoluble-residue materials in the dolostone are as same as REE patterns of the upper continental crust (UCC); the other samples are enriched in HREE. During weathering processes, the REE patterns of bedrock-cracked rock-silty rock in the dolostone profiles are characterized by arise in total REE, increment in $(\text{La}/\text{Yb})\text{N}$ and negative Ce anomalies. Nd and Sr isotopic compositions of carbonate rocks clearly distinguish Cambrian dolostone ($^{87}\text{Sr}/^{86}\text{Sr}=0.708135$, $\epsilon_{\text{Nd}}(0)=-13.69$) from almost Triassic carbonate rocks ($^{87}\text{Sr}/^{86}\text{Sr}=0.708016-0.708927$, $\epsilon_{\text{Nd}}(0)=-8.35--10.73$), with the exception of the Triassic dolostone with peculiar REE patterns has high values ($^{87}\text{Sr}/^{86}\text{Sr}=0.709577$, $\epsilon_{\text{Nd}}(0)=-6.22$). In the $\epsilon_{\text{Nd}}(0)$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ diagram[4] of insoluble-residue materials in carbonate rocks, all the samples fall within the range of old sediments, and clearly distinguish dolostone from limestone. A striking change in Sm/Nd ratios for silty rock-cracked rock-bedrock in the dolostone profiles can be observed, which could lead to a change in Nd isotopic composition. An interesting positive relationship between $\text{Nd}(0)$ vs. $147 \text{ Sm}/^{144}\text{Nd}$ can be observed as in the cracked rock-bedrock and insoluble-residue materials of dolostone. This relationship is almost similar to that obtained by Goldstein and Jacobsen (1988)[5] and Allègre et al., (1996)[6], from a variety of world-wide rivers. Based on the above results, it is believed that the limestone and dolostone were formed in various marine environmental backgrounds, and it did not support the concept of dolomitization by seawater in shallow-water carbonate platforms. The insoluble-residue materials in carbonate rocks were derived from multi-recycled and well-mixed old sediments, and they can provide valuable information about the average chemical composition of the upper continental crust.

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