UPPER PRECAMBRIAN DOLOMITES FROM CRISÓPOLIS (BAHIA): CHEMICAL AND PETROGENIC STUDY

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ABSTRACT The Crisópolis dolomite, Northern Bahia, occurs in a limited vertical sequence of predominantly dark-coloured compact dolomite strata containing minor beds of lighter oolitic-rich siliceous dolomite and rare chert partings. This sequence, believed to be of Upper Precambrian age, has undergone low-grade metamorphism. Mineralogically, the rocks consist of dolomite, quartz and talc. Chemical data show an overall abundance of silica with clear signs of metasomatic diffusion in the compact dolomite strata. Sodium content decreases as silica metasomatism increases. Detrital and/or hydrolized elements like Fe, Mn, Ti, Zr and K are present in minor amounts. A model for the genesis of the dolomite proposes:

- a) deposition of primary CaCO_3 and magnesian calcite from water which is probably a little hypersaline;
- b) dissolution of primary carbonates at lower pH conditions and reprecipitation of dolomite with extensive sweating out of more soluble CaCO_3 ;
- c) contemporaneous silica precipitation and its metasomatic diffusion during the diagenetic stage.

A paleo-environmental model is proposed. Accordingly, the primary carbonate deposition would have occurred in an intertidal zone and the dissolution-reprecipitation stabilization of carbonates related to the interference of meteoric waters.

RESUMO As rochas dolomíticas de Crisópolis, nordeste da Bahia, ocorrem em uma sequência vertical limitada, consistindo predominantemente de camadas compactas de dolomito escuro contendo finas camadas mais claras de dolomito silicoso oolítico e raras concreções silicosas. Essa sequência é presumivelmente de idade pré-cambriana superior e apresenta um metamorfismo de baixo grau. Mineralogicamente as rochas são constituídas principalmente de dolomita, quartzo e talco. As camadas compactas de dolomito apresentam uma abundância de sílica com evidências claras de difusão metassomática. O teor em sódio diminui com o aumento da sílica metassomática. Os elementos detriticos e/ou hidrolizados, como o Fe, Mn, Ti, Zr e K, estão presentes em quantidade menores. Um modelo genético da dolomita propõe:

- a) deposição de CaCO_3 e calcita magnesiana a partir da água, que é provavelmente um pouco hipersalina;
- b) dissolução dos carbonatos primários em condições de pH mais baixas e reprecipitação de dolomita com extensa exsudação do CaCO_3 mais solúvel;
- c) precipitação contemporânea da sílica e difusão metassomática da mesma durante o estágio diagenético.

É proposto um modelo paleoambiental, segundo o qual a deposição do carbonato primário teria ocorrido em uma zona intermaré. A dissolução bem como a reprecipitação e estabilização dos carbonatos estariam relacionadas com a ação de águas meteóricas.

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INTRODUCTION Precambrian dolomitic carbonate rocks are widespread in the Bahia State. Genetically, they may be divided into three main groups: the first comprises recrystallized impure carbonate rocks incorporated in the Archean-Lower Proterozoic basement formations; the second group consists of an extremely extensive group (the Bambuí Group) of Upper Precambrian age stretching in a N-S and E-W direction in North-Central Bahia; the third group comprises minor carbonate sequences widely distributed in Upper Precambrian formations. No mineralogical or chemical data whatsoever are available on this last group of carbonate rocks, and its genesis is accordingly unknown.

This paper presents mineralogical and chemical data on a minor dolomitic sequence occurring near Crisópolis, and offers a genetic interpretation. The findings of the present study may also throw light on the genesis of other Upper Precambrian carbonate formations, including the extremely important Bambuí Group.

GEOLOGICAL NOTES The carbonate sequence in question outcrops near Crisópolis, northern Bahia, Brazil.

It corresponds to the bottom of Estância formation (Allard e Tibana, 1963), probably of the Upper Precambrian age, correlated to the Bambuí Group (Humphrey e Allard, 1969). Dolomitic rocks have been found resting directly on the Lower-Precambrian basement.

The sequence studied is about 60 m thick and consists of a succession of larger compact dolomitic strata varying in thickness between 0,5 and 2 m and interlayered with thinner, lighter dolomites. Thin layers of light grey-coloured material of schistous aspect are sometimes present on top of the massive dolomite strata. The colour of the dolomitic rocks varies from light-grey to dark-grey, even within a single dolomite stratum (see the Fig. 1). Chert partings are rare and irregularly distributed.

Structures of *Collenia* algae (Allard e Tibana, 1963; Humphrey e Allard, 1969) are visible in some outcrops.

Figure 1 — Sketch map of the stratigraphic column of the Crisópolis dolomite. D = dark dolomite; L = light dolomite; T = talcous level; O = oolite-rich level

MINERALOGICAL AND PETROGRAPHIC FEATURES 22 samples, including massive dolomites, oolite-bearing samples and schistous material were studied. 19 samples (including a chert sample, CR 16) were taken from the above-described sequence. They are numbered according to their point of collection starting from the bottom of the formation (Fig. 1). The remaining three samples were collected from other carbonate series in neighbouring areas. In thin section, massive dolomites are seen to consist of a mixture in varying proportions of a microcrystalline matrix and of larger carbonate and quartz crystals. Oolites, pellets, etc. may be present in general as fragments but are relatively rare.

Recrystallization of the microcrystalline matrix and of the larger crystals is frequently advanced or total, thus making it impossible to deduce with any accuracy the nature of the original material. Quartz is present in large quantities in most parts of the formation, so it can be called siliceous dolomite. Quartz crystals do not exhibit detrital features but are present in the form of well-crystallized grains which fill the pores and microfractures of the rock, cement crystals of different nature and replace previous structures (dolomite crystals, oolites, etc.). In some cases, the quartz content varies progressively within a massive stratum. More frequently, it varies discontinuously, as can be observed macroscopically, the more siliceous dolomites being light in colour.

Several features indicate that the metasomatic silica diffusion was a relatively early process occurring during a diagenetic stage, as has frequently been observed (Ingerson, 1962). Dolomite is also largely recrystallized both in the fine micritic matrix and as larger crystals. Analysis by X-ray diffraction indicates that carbonates consist wholly of dolomite. While detrital quartz is practically absent, in some samples (CR 9 and CR 10) fragments of dolomite crystals with detrital features are recognizable. In these samples, remnants of material of probable organogenic origin, like pellets and algal fragments, are also visible. Three strata of light-coloured dolomite (CR 1, CR 11 and CR 14a) are extremely rich in oolites which have largely been replaced metasomatically by quartz.

Those not metasomatized present radial or concentric structures. Post-depositional processes that might have introduced mineralogical changes include diagenesis and low-grade metamorphism. Talc, which is everywhere present in the massive dark-or light-coloured dolomite and schistous interlayers, is, of course, of metamorphic origin. Alignments of talc crystals frequently develop at the contact between fine readsorbed quartz-rich layers and dolomite. It is the end product of a metamorphic reaction of the type:

the experimental conditions of which are known (Metz and Trommsdorff, 1968; Turner, 1967; Thompson, 1975). Talc is strongly concentrated in the sample CR 8, which is a thin schistous layer a few cm thick sandwiched between two large dolomite strata.

GEOCHEMICAL PATTERNS Geochemical data for 22 samples (including a chert sample) are reported in Table 1. Major variations in the chemistry of carbonate rocks are related to the percentage of the non-carbonate fraction and also involve the Ca/Mg ratios. Most of the samples that consist largely of carbonates have molecular Ca/Mg ratios a little below unity. The Ca/Mg ratios decrease markedly in the silica-rich samples (Fig. 2) thus confirming the strong magnesian character of the entire formation. As regards elements other than Ca and Mg, the geochemistry of carbonate rocks is complicated by the observation (e.g. Graf, 1962) that most of these elements strictly depend on the non-carbonate materials that may have been deposited with carbonates by any one of several different processes, for it may have been incorporated in carbonates either as a detrital component,

Table I — Main features and chemical data for the Crisópolis carbonate rocks

Sample	Remarks	Tot. ign. loss 950°	CO ₂ (volum.)	H ₂ O ⁺	carbon. % (as dolom.)	Ca/Mg (mol.)	SiO ₂
Cr 1	light colour., calc. oololiths	40.70	36.57	4.13	85.11	0.80	13.48
CR 2	very dark, total recryst	46.51	43.77	2.74	97.26	0.88	1.00
CR 3	very dark, total recryst	46.28	44.12	2.16	96.77	0.89	0.90
CR 4	light, total recryst., talc	40.36	37.23	3.13	84.39	0.63	14.50
CR 5	dark, cryptocrystalline	45.07	41.76	3.31	94.24	0.85	6.30
CR 6	light, talc	36.43	32.65	3.78	76.18	0.59	21.75
CR 7	dark, partial recryst., talc	40.19	38.80	1.39	84.04	0.70	17.75
CR 8	light, talc, oololiths	28.02	22.65	5.37	58.59	0.44	34.38
CR 9a	dark, partial recryst., talc	43.70	40.68	3.02	91.38	0.71	7.34
CR 9b	very dark, cryptocrystalline	43.83	40.61	3.22	91.65	0.79	8.70
CR 10	very dark, total recryst.	43.70	42.94	0.76	91.38	0.92	6.86
CR 11	light, oololiths, talc	35.54	33.13	2.41	74.32	0.76	25.94
CR 12	dark, partial recryst.	43.38	41.72	1.66	90.71	0.82	8.17
CR 13a	dark, cryptocryst., talc	43.08	39.23	3.85	90.08	0.72	5.56
CR 13b	light partial recryst., talc	30.03	26.56	3.47	62.79	0.47	29.23
CR 14a	white, oololiths, talc	20.36	16.54	3.82	42.57	0.31	47.40
CR 14b	dark, partial recryst., talc	39.07	38.21	0.86	81.70	0.61	18.03
CR 15	dark, partial recryst.	43.14	42.15	0.99	90.21	0.69	5.58
CR 16	chert, 3-25 cm thick	9.80	9.63	0.17	20.49	0.32	78.65
CR 17	very dark, algal fragments	43.99	43.84	0.15	91.99	0.93	8.66
CR 18	dark, algal fragments	46.77	45.86	0.91	99.16	0.82	0.08
CR 19	dark, algal fragments	44.19	42.31	1.88	92.40	0.82	8.16

Sample	TiO ₂	Al ₂ O ₃	Total Fe (as Fe ₂ O ₃)	MnO	K ₂ O	Na ₂ O	P ₂ O ₅	Sr ppm	Zr ppm
Cr 1	0.01	0.51	0.157	0.010	0.035	0.37	0.09	85	10
CR 2	0.01	0.19	0.090	tr	0.040	0.90	0.08	62	10
CR 3	tr	0.10	0.090	0.010	0.010	0.38	0.07	45	10
CR 4	0.05	1.15	0.23	0.010	0.025	0.05	0.07	40	10
CR 5	0.01	0.22	0.136	0.012	0.032	0.04	0.07	5	10
CR 6	0.05	0.75	0.75	0.010	0.064	0.45	0.07	55	10
CR 7	0.02	0.41	0.134	0.010	0.026	0.10	0.06	35	10
CR 8	0.23	3.90	1.43	0.010	0.37	0.11	0.08	30	31
CR 9a	0.23	0.11	0.093	0.014	0.019	0.20	0.07	58	10
CR 9b	0.02	0.45	0.103	0.010	0.023	0.09	0.07	55	10
CR 10	0.02	0.50	0.189	0.011	0.060	0.36	0.07	45	10
CR 11	0.01	0.16	0.108	0.010	0.017	0.21	0.06	35	10
CR 12	0.01	0.19	0.162	0.018	0.033	1.18	0.08	53	10
CR 13a	0.02	0.30	0.205	0.020	0.043	0.28	0.23	50	10
CR 13b	0.01	0.21	0.146	0.010	0.007	0.10	0.04	33	10
CR 14a	0.03	0.55	0.323	0.010	0.020	0.51	0.01	10	10
CR 14b	0.01	0.22	0.256	0.010	0.048	0.54	0.06	42	10
CR 15	0.04	0.65	0.230	0.010	0.07	0.13	0.07	45	10
CR 16	0.02	0.90	0.42	0.010	0.032	0.22	0.01	5	10
CR 17	0.01	0.14	0.114	0.020	0.014	0.06	0.06	62	10
CR 18	0.01	0.10	0.143	0.025	0.024	0.73	0.07	41	10
CR 19	0.01	0.48	0.231	0.010	0.036	0.84	0.07	40	10

or by chemical precipitation from sea water in a simple or complex ionic form, or by biochemical mechanism. The elements typical of the hydrolizates like Al, Fe, Ti and Zr probably derive from small quantities of terrigenous material, incorporated in the carbonates. The highest concentrations of Fe and Mn in carbonate rocks are frequently associated with clastics of land derivation (Button, 1974). On the other hand, they may, together with other divalent element (Zn, Cd, etc.), be present in sea water as dissolved carbonates and co-precipitate with CaCO₃ because of their lower solubilities (Crocket and Winchester, 1966).

Figure 2 — Variation of the molecular Ca/Mg ratio with silica content

The concentration of these elements in sea water may thus be controlled by their carbonate form instead of by precipitation as pure compounds, as has been suggested (Krauskopf, 1956; Goldberg, 1967), or by organic complexing and biochemical mechanisms. In the case of the Crisópolis dolomite, iron is roughly but significantly correlated with alumina, a compound known to be related to the hydrolizate fraction. This seems to exclude the possibility of iron being chemically precipitated with calcium from sea water, as sometimes suggested (Truswell and Eriksson, 1975). A remarkable feature of the present carbonates when compared with other carbonates with similar silica content (see e.g. Weber, 1964 a; Turekian and Wedepohl, 1961; Graf, 1962), is the scarcity in most samples of elements of the non-carbonate fraction (Al, Ti, K, etc.). This poses problems concerning the origin of the silica which will be discussed later. Sodium (average content 0,27%) is markedly higher than in other dolomites and dolostones (Weber, 1964a), and since most of it (sodium) cannot be genetically correlated to the limited non-carbonate fraction it may have been precipitated from seawater of somewhat higher salinity, a situation often suggested by stratigraphic and paleogeographical studies (Weber, 1964b). In this case, appreciable amounts of sodium may remain trapped in the liquid inclusions of the sediments. It is worthy of note that in the massive dolomite strata the sodium content, normally decreases as silica increases, an observation that will have a bearing on the discussion of the silicification process of the Crisópolis dolomite. Strontium abundances (average content 42 ppm) are notably less than the concentration ranges found in limestones (Graf, 1962) and dolostone (Weber, 1964a). It should be noted that depletion of strontium in carbonate rocks seems to characterize every recrystallization process of primary crystallized carbonates, both in the sedimentary diagenesis and in metamorphic recrystallization (Robinson, 1971; Thompson, 1972). Sample Cr 8 contains much more Al, Fe and K, which have probably been derived from terrigenous compounds brought into the sedimentary basin as fine argillaceous material.

GENESIS AND POST DEPOSITIONAL HISTORY OF THE CRISÓPOLIS DOLOMITE The crucial points to be investigated in the genetical reconstruction of the Crisópolis dolomite are: a) the environmental conditions for the primary precipitation

of carbonates, b) its conversion into dolomite, c) the origin of the silica and d) the mode of metasomatic silicification of previous carbonates. The dependence of the Ca/Mg ratio on the silica content of the rock indicates that the genetical process of the present carbonates was closely connected with silicification. The origin of the sedimentary dolomite has long been and still is a controversial subject. Geological and isotopic studies (see e.g. Degens and Epstein, 1964; Weber, 1964b) indicate that dolomite would have formed in the initial stages of salt deposition or in the diagenetic stages. Two main hypotheses must be considered: a) direct precipitation of dolomite from sea water under evaporitic conditions (Ingerson, 1962; Peterson *et al.*, 1963; Weber, 1964b) or from hypersaline brines (Friedman and Sanders, 1967). In this context it should be noted that high Mg/Ca ratios of solutions are also thought to favour primary precipitation of dolomite (Sass, 1965; Lebedev, 1965), and additional findings (see e.g. Glover and Sippel, 1967; Clayton *et al.*, 1968) confirm the possibility of primary precipitation of dolomite in lagoonal or lacustrine environments even under non-evaporitic conditions; b) some sort of metasomatism of preexisting calcium carbonates. This hypothesis is strongly supported by carbon and oxygen isotope data (Degens and Epstein, 1964).

The difficulty of forming dolomite structures even hydrothermally (Epstein *et al.*, 1962) suggests that dolomite does not crystallize in a finite time. For this reason, most authors retain that all low temperature dolomites are secondary. Opinions differ as to how dolomitization proceeds. It is generally accepted that primary carbonates precipitating from sea waters under alkaline conditions are aragonite and high-magnesium calcite. Thermodynamic considerations show that dolomite is stable in normal sea water at 25° with respect to CaCO₃ and magnesian calcites. According to Truswell and Eriksson (1975), stabilization takes place via one of the following diagenetic processes:

- i) the earliest carbonates underwent dissolution because of a lowering of the environmental pH and replacement and reprecipitation as calcite and/or dolomite took place;
- ii) aragonite in the solid state to calcite, or high-magnesium calcite exsolves to calcite and dolomite (Land, 1967);
- iii) the replacement dolomitization process is enhanced by an increased Mg/Ca ratio of the dolomitizing solutions.

The first hypothesis is of greater interest in that it has a bearing on the behaviour of silica. In conditions conducive to the precipitation of carbonates, amorphous silica is soluble, particularly at pH's values above 8 (Eugster and Ming Chow, 1973). The pH of the interstitial waters of carbonate sediments is above 9 (Krauskopf, 1967), hence they contain large quantities of dissolved silica (Emery, 1960). If, during dolomitization the environmental pH is lowered, silica becomes saturated in solution and precipitated as calcedonic silica or quartz, depending on their absolute concentration in solution (Versey, 1939; Kolodny *et al.*, 1965; Oldershaw, 1968). The rare replacement cherts present in the Crisópolis series are probably related to such a mechanism. Regarding the massive proportions of silica present throughout the entire carbonate series, a number of observations lead one to exclude the possibility of its having been precipitated from the interstitial waters of the sedimentary pile. Firstly, the amount of silica present is far in excess of that suggested by silica solubility data in marine waters (Krauskopf, 1956). Secondly, the inverse correlation between silica and sodium (being this last element have been trapped in the interstitial waters) proves that silica metasomatism proceeds with the expulsion of interstitial water. The bulk of the silica must, therefore have an origin foreign to the carbonate sediments. A number of hypotheses regarding the origin of the silica can be put forward:

1. silica was brought into the sedimentary basin as fine detrital quartz of land-derivation;
2. soluble silica was removed by biological uptake (Okamoto *et al.*, 1957) involving phytoplankton and the species Diatomeaes and Radiolaria, which are widespread in extremely varied habitats (Parea, 1970) Siliceous skeletons may then have precipitated directly into the carbonate mud or may have been dissolved and later precipitated as colloidal silica, depending on physical variables (pH, concentration, etc.);
3. at the boundary between continental and marine waters silica was inorganically removed by adsorption in suspended solid or colloidal material (Huang, 1975).

The first hypothesis, namely that the bulk of silica is of continental derivation, and which at first sight affords the simplest explanation, fails to take into account the fact that silica is not accompanied by discrete amounts of other detrital elements.

A point of a certain interest is the fact that the silica — rich samples are much more strongly magnesian in character than pure carbonate rocks. This correlation cannot be easily explained. The causes must clearly be sought in the particular conditions of the primary deposition of carbonates or in the diagenetic process, for lowgrade metamorphism is incapable of introducing such pronounced changes in the Ca/Mg ratio of carbonate rocks.

A PALEO-ENVIRONMENTAL MODEL In the case of the Crisópolis dolomites, any paleo-environmental reconstructions, based on Irwin's (1965) limestone shelf model, must take into account the strongly magnesian character of carbonates, the presence of a great amount of silica and the significance of the non-carbonate fraction. In general, strongly magnesian marine waters which may determine low values for the Ca/Mg ratio of carbonates are encountered in shallow epeiric seas of high surface to volume ratio (Gaines, 1968). Similar environments (shallow-water areas and evaporitic settings) are also the preferred removal sites for silica (Holland, 1972). The proposed mechanisms for dolomite formation, silica precipitation and silification of carbonates imply variations in the environmental pH conditions during the deposition and diagenetic stages of carbonates. The establishment of the causes that have produced such variations in the pH is fundamental for the choice of a paleo-environmental model. Displacement to more acid pH may occur when the earliest carbonates either become subaerially exposed (Purdy 1965), or come into contact with meteoric waters (Blatt *et al.*, 1972; Badiozamani, 1973). According to Truswell and Eriksson (1975), dolomitization may occur both in the subtidal and intertidal zone of Irwin's model. In the subtidal zone, the interstitial waters remain alkaline in character, dissolution of the earliest carbonates and precipitation of silica thus being rendered difficult. This means that dolomitization rarely enhances saturation and the rock is essentially silica free. In the intertidal zone, dolomite saturation would be achieved through an influx of meteoric waters which would favour, on one hand, the dissolution of the earliest carbonates (Badiozamani, 1973) and on the other, the precipitation of silica. From this it is evident that an intertidal zone is the most suitable for the formation of the Crisópolis carbonate series. The presence of fragmented material and of thin oolite-rich layers within the massive carbonate strata indicate that the primary deposition of carbonates underwent interruptions in time and that, contemporaneously, material removed by erosion from the barrier of Irwin's limestone shelf model was accumulated in the intertidal zone. According to such a reconstruction, water of continental provenance would have played the major role in lowering the pH in the carbonate basin and hence in accelerating the diagenetic process.

Further study on the carbon and oxygen isotopic composition of the dolomitic rocks might serve to verify the validity of the proposed model.

ANALYTICAL NOTES The element iron, Mn, K and Na were determined by atomic absorption spectroscopy. Other major and trace elements were determined by X-ray fluorescence according to Franzini and Leoni (1972). Loss on ignition at 950° was determined on 2-g samples. Volumetric determination for CO₂ were made.

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