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QUIMIOESTRATIGRAFIA DE ISÓTOPOS DE C E Sr DE MÁRMORES DO COMPLEXO SÃO CAETANO, ZONA TRANSVERSAL, PROVINCIA ESTRUTURAL DA BORBOREMA: IMPLICAÇÕES REGIONAIS E GLOBAIS

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Dissertação que apresentou ao Programa de Pós-Graduação em Geociências do Centro de Tecnologia e Geociências da Universidade Federal de Pernambuco, orientada pelo Prof. Alcides N. Sial., em preenchimento parcial para obter o grau de Mestre em Geociências, área de concentração Geologia Sedimentar e Ambeintal , defendida e aprovada com distinção em 21 de junho de 2004.

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A meus pais pelo seu constante amor e apoio (A mis padres por su constante amor y apoyo).
A Wanessa quem ter-me oferecido amor incondicional.

APRESENTAÇÃO

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RESUMO

A composição isotópica de mármores do Complexo São Caetano (CSC), municípios de Flores e Afogados da Ingazeira, Pernambuco, foi usada para se estimar a idade de deposição das seqüências carbonáticas originais (protolito dos mármores) e para se investigar mudanças na composição global da água do mar durante sua deposição. Após comparar-se a curva de variação secular de isótopos de C e Sr para estas sucessões carbonáticas com curvas para seqüências de carbonatos sedimentares bem conhecidas a nível mundial, uma idade Meso-Neoproterozóica (1,1-0,97 Ga) é proposta para a deposição dos carbonatos do CSC.

Três diferentes estágios isotópicos (I, II, III) foram definidos e correlacionados com eventos globais que teriam afetado a composição da água do mar durante a transição Meso-Neoproterozóico (1,1-0,97Ga.). Um estagio inicial (I), com valores moderadamente altos de $\delta^{13}C$ (~ +3,7‰$_{PDB}$) que refletem um aumento no seqüestro e soterramento do carbono orgânico, associado a um extensivo crescimento crustal ocorrido no auge do ciclo orogênico Grenvilliano. O estagio isotópico II, apresenta valores mais variareis de $\delta^{13}C$, entre -2 e +3‰$_{PDB}$, interpretados como devido ao aumento no aporte de CO_2 rico em ^{12}C associado a um evento de riftamento global há 1,05 Ga e ao seqüestro de matéria orgânica rica em ^{12}C através de subdução e formação de arcos magmáticos a nivel global há ~1,0 Ga respectivamente. O estagio isotópico III, com valores de $\delta^{13}C$ em torno de +3,7‰$_{PDB}$, evidencia uma continua sedimentação e concomitante soterramento da matéria orgânica, associada `a aglutinação do supercontinente Rodinia. A quimioestratigrafía de isótopos de Sr, com valores de $^{87}Sr^{86}Sr$ ~0,706 caracterizando o estagio isotópico I, valores um pouco mais variáveis (de 0.706 a 0,707) no estágio isotópico II, e valores em torno de 0,706 caracterizando o estágio isotópico III, apóiam estas idéias.

Baseados no intervalo de idade de deposição aqui proposto e em relações geológicas regionais, é possível propor-se que os protólitos sedimentares dos mármores do CSC ter-se-iam depositado após um evento de riftamento na Zona

Transversal da Província Borborema entre 1.4 e 1.05 Ga. Características litológicas da parte siliciclástica do CSC indicam, por outro lado, que este ter-se-ia depositado numa margem continental em ambientes pelágicos. A margem continental, onde foram depositados os sedimentos do CSC foi estabelecida ao norte do Craton São Francisco e suas supracrustais Meso-Paleoproterozóicas associadas. A sedimentação do CSC foi interrompida pela convergência oceânica-continental (subdução) que levou a formação de arco magmático Cariris Velhos. Comparações das curvas isotópicas de variação secular do CSC com as propostas em seqüências sedimentares bem preservadas, indicam que os protolitos dos mármores estudados teriam-se depositado durante um período de subida do nível do mar.

Por outro lado, levando-se em consideração que a composição isotópica de C e Sr de carbonatos pode ser alterada por processos pós-deposicionais (e.g diagênese e metamorfismo), possíveis alterações da assinatura isotópica original dos carbonatos (mármores) do SCC, foram investigadas por metodologia multivariada, incluindo: (1) caracterização petrográfica, (2) caracterização dos elementos (elementos maiores e menores), e (3) determinação da composição isotópica dos carbonatos e grafitas associados.

Concluiu-se que a alteração da assinatura isotópica de C encontrada em algumas das amostras estudados esta associada à presença de grafita. Uma difusão entre CH_4 rico em ^{12}C (derivado da grafita) e os carbonatos é proposta como o mecanismo que afetou a composição isotópica dos carbonatos, causando diminuições em seus valores de $\delta^{13}C$ em ambiente fechado durante o metamorfismo. Isto é apoiado pela pouca variação dos valores de $\delta^{18}O$ e $^{87}Sr/^{86}Sr$; como também pela natureza inalterada dos indicadores de elementos geoquímicos (conteúdos de Sr com media de 1500 ppm, razões de Mn/Sr de 0.006 até 0.140, e razões de Rb/Sr entre 0 e 0.005). Este processo ocorreu sob condições de metamorfismo de baixa pressão e media temperatura, como é apoiado pela paragênese dos mármores (calcita, quartzo, tremolita, moscovita, diopsidio e granada), as quais indicam temperaturas na faixa de 500-700^{0}C. O Intervalo de temperatura para o metamorfismo (514 e 750^{o}C) calculado a partir o termômetro calcita-grafita apóia esta idéia.

ABSTRACT

C-, O- and Sr-isotope composition from marbles successions of the São Caetano Complex (SCC), located near Flores and Afogados da Ingazeira towns, state of Pernambuco, were used to constrain the depositional age of the original carbonate sequences (marble precursors) and to contribute to the understanding of the possible factors affecting the global geochemistry of ocean water during their deposition. After contrasting C and Sr-isotope secular variation curves from the SCC marbles with those of well known carbonate sequences worldwide, a Meso-Neoproterozoic age (1.1-0.97 Ga) is here proposed for the deposition of the original limestone sequences.

Three different C-isotope stages (I, II, III) were determined based on the C-isotope secular variation pathways, and correlated with major global events, which would have affected the C-isotope composition of the Meso-Neoproterozoic seawater (1.1-0.97 Ga.). An initial stage (C-Isotope stage I), shows moderately high $\delta^{13}C$ values (~+3.7‰$_{PDB}$) which would have resulted from an increasing sequestration of organic carbon by enhanced burial associated to the large continental growth occurring during the onset of the Grenville orogenic cycle. The C-Isotope stage II, has $\delta^{13}C$ values displaying stronger oscillations (from -2‰ to +3‰$_{PDB}$). The negative values may reflect the enhanced mid-oceanic volcanism and the ^{12}C-rich CO_2 release into the ocean during a global rifting event occurring at 1.05 Ga. The positive values reflect the ^{12}C-rich organic carbon sequestration through subduction, which would have been associated to widespread continental arc formation at ~1.0 Ga. The C-isotope stage III, which displays $\delta^{13}C$ values around 3.7‰$_{PDB}$, would have reflected a continued sedimentary organic burial associated to the agglutination of Rodinia Supercontinent.

The Sr-isotope chemostratigraphy with constant $^{86}Sr/^{87}Sr$ values (~0.706) characterizing C-isotope stage I, slightly fluctuating values (from 0.706 to 0.707) characterizing C-isotope stage II and $^{87}Sr/^{86}Sr$ values averaging 0.706 characterizing C-isotope stage III, further support this idea.

Based on the depositional age determined for the studied marbles, it is proposed that their sedimentary precursor would have been deposited after a rifting event occurring in the Transversal Domain of the Borborema structural domain between 1.4-1.05 Ga. Lithological characteristics of the SCC silicilcastic successions indicate, on the other hand, that the SCC should have been deposited in a pelagic environment, along a continental margin. Comparisons between the $\delta^{13}C$ values from the SCC and those from well-preserved sedimentary sequences indicate that the original limestone successions would have been deposited during a period of global sea level rise.

Regional relationship with other lithologic units, on the other hand, allow to propose that such a continental margin would have been located north of the São Francisco craton and related Paleo and Mesoproterozoic supracrustal entities. Ocean closure related to ocean-continent plate convergence and subduction, the latter allowing the formation of a continental arc (Cariris Velhos) at 0.96 Ga, put end to the sedimentation of the SCC.

Since the C-and Sr-isotope composition of carbonate sequences can suffer post-depositional alterations during diagenesis or modified by metamorphism, possible alterations of original isotope signature of SCC marbles were investigated by using a multivariable approach, which includes: (1) petrographic characterization, (2) elemental characterization (major and minor elements) and (3) determination of isotope composition of carbonates and graphite.

Based on this multivariable approach, it was concluded that the post depositional alteration of original carbonate C-isotope signature of some samples presenting depleted $\delta^{13}C$ values was associated to the presence of graphite and to the concomitant graphite derived ^{12}C-rich CH_4 - carbonate diffusion process. Such an isotope modification would have occurred under buffered conditions in which the action of external fluids was negligible. This is supported by the only slightly variable $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ values and the unaltered nature of the elemental indicators (Sr contents averaging 1500 ppm, Mn/Sr ratios from 0.006 to 0.140, and Rb/Sr ratios between 0 and 0.005). This process would have occurred during low pressure–medium temperature conditions. This is supported by the petrologic paragenesis (calcite, quartz tremolite, muscovite, diopside, garnet) that indicate temperatures between 500 and 700^{0}C and metamorphism temperatures from 514 to 750^{o}C determined from C-isotope thermometry of coexisting calcite and graphite.

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INTRODUÇÃO

Desde o trabalho pioneiro de Harold Urey (1932) no qual a existência de dois isótopos de hidrogênio foi determinada por meios espectrométricos, o uso de isótopos estáveis tem ganhando uma ampla aceitação entre a comunidade cientifica. O continuo aprimoramento das técnicas analíticas neste ramo da geoquímica, conjugado ao desenvolvimento de novas aplicações das mesmas nas Ciências da Terra, tem permitido alcançar uma alta aplicabilidade e versatilidade na interpretação dos processos geológicos, climáticos, biológicos e até extraterrestres que teriam controlado a evolução do nosso planeta.

Isótopos estáveis de O, C, H, S, Fe entre outros, tem sido os mais amplamente empregados em pesquisas geocientíficas. Uma das aplicações que mais tem revolucionado a pesquisa geológica é a quimioestratigrafía de isótopos estáveis de C e O, e ultimamente S, em seqüências carbonáticas, a qual é complementada com analises de isótopos de Sr (Kaufman et al., 1991, Sial et al., 2000, Kah et al., 2001). Apesar de esta ser uma técnica que foi desenvolvida durante os anos setenta (e.g. Veizer e Hoefs, 1976) e aplicada na área de exploração do petróleo nos anos oitenta (e.g. Scholle e Arthur, 1980; Mitchell et al., 1996), a implementação da quimioestratigrafía em a caracterização geoquímica de seqüências carbonáticas tanto sedimentares quanto metamórficas, alcançou seu maior desenvolvimento na primeira metade dos anos noventa (Veizer et al., 1989a,b, 1990, 1992, Derry et al., 1992, Kaufman et al., 1991, Kaufman e Knoll, 1995, entre outros). Assim, esta aplicação tem ganhado grande quantidade de adeptos uma vez que permite a determinação de idades de deposição de seqüências carbonáticas com grande precisão, como também a caracterização geoquímica de ambientes sedimentares a partir dos quais seqüências carbonáticas se depositaram (geoquímica de oceanos, lagos, etc).

A mais importante utilidade da quimioestratigrafía, no entanto, centra-se na possibilidade de avaliar possíveis fatores que afetaram a geoquímica da água do mar através do tempo geológico, tanto global quanto regionalmente (Veizer et al., 1989a,b; Jacobsen e Kaufman, 1999; Hayes et al., 1999; Sial et al, 2000; Lyndsay e Brasier, 2002; Bekker et al., 2003). Ė desta perspectiva que a aplicabilidade da quimioestratigrafía tem-se tornado ainda mais valiosa. Caracterizações multivariadas da composição isotópica de diferentes materiais (carbonatos, fosfatos, sulfetos, sulfatos, etc) têm permitido avaliar e diferenciar como os processos geológicos, climáticos e biológicos têm modificado de forma conjunta e/ou separada a geoquímica dos oceanos através do tempo (Des Marais, 1994; Lyndsay e Brasier, 2002; Bekker et al., 2003, Bartley et al., 2001, Kah et al., 1999; Bartley e Kah, 2003, Frank et al., 2000, 2003; Hoffman et al., 1998 a, b; Hoffman, 1999, Halverson et al., 2003). Alem disso, a quimioestratigrafía tem permitido avaliar mudanças nos ciclos biológicos e biogeoquímicos ao ser conjugada com outras linhas de pesquisa tais como paleontologia, sedimentología e estratigrafía de seqüências (Scholle e Arthur, 1980; Mitchell et al., 1996, Kah et al., 1999; Des Marais, 1997).

Por outro lado, a quimioestratigrafía de isótopos estáveis tem permitido correlacionar seqüências de carbonatos sedimentares ou metamórficos de diferentes localidades com diferentes intervalos de idade, independentemente da história geológica sobreposta neles. Neste sentido a quimioestratigrafía de isótopos estáveis mostra maior versatilidade, já que determinações deste tipo em seqüências metamorfizadas apresentam dificuldades devido à falta de indicadores geocronológicos confiáveis. Desta forma, dificuldades anteriormente experimentadas na correlação de seqüências em diferentes ambientes geológicos é superada e reconstruções de eventos geológicos globais tornam-se ainda mais amplamente apoiadas (Melezhik et al., 1997, 1999, 2001, Knoll et al., 1995; Frank et al., 1997, Kah et al., 1999; Kah et al., 2001; Bartley et al., 2001; entre outros). Em estudos que envolvem seqüências carbonáticas precambrianas, onde faltam indicadores geocronológicos (fósseis) e uma grande diversidade de eventos pós-deposicionais são superpostos (metamorfismo e diagênese avançada), a aplicabilidade da quimioestratigrafía de isótopos de C, O e Sr é ainda mais útil já que permite avaliar condições paleoclimáticas, paleogeográficas, paleobiológicas e paleotectônicas independente dos eventos pós-deposicionais e o escasso registro sedimentar durante o período (Bartley et al., 2001, Kah et al., 1999, Hoffman et al., 1998ª,b; Hoffman, 1999, Bekker et al., 2003).

Por outro lado, a aplicação de isótopos estáveis de carbono e oxigênio não tem sido restrita somente à realização de trabalhos quimioestratigráficos, mas tamben, para avaliar processos pós-deposicionais que afetam o registro sedimentar e as características isotópicas originais destes (Veizer, 1893, Brand e Veizer, 1980a,b, Kaufman et al., 1991). Esta aplicabilidade tem dado uma ampla versatilidade a sua utilização na pesquisa geológica, ajudando não somente a melhorar a resolução das análises quimioestratigráficos, mas também a resolver outro tipo de questões na área das Geociências, como por exemplo, determinações de condições diagenéticas e metamórficas, tipo e grau de fluxo de fluidos durante estes processos, paleotermometría, determinação de variações na composição isotópica das águas subterrâneas entre outras (Kaufman et al., 1991; Melezhick et al., 2001; Valley, 2001; Evans et al., 2002).

Com fins quimioestratigráficos, determinações de eventos pós-deposicionais ajudam a identificar os processos ocorridos durante os diferentes estágios de evolução de rochas carbonáticas. Vários trabalhos têm demonstrado que variações na composição isotópica dos carbonatos é favorecida durante diagênese e/ou metamorfismo por fatores como: (1) presença de minerais cuja composição inclui carbono ou favorece a formação de carbono durante esses eventos, (2) presença de fluidos intersticiais ou intercristalinos contendo uma assinatura isotópica diferente dos carbonatos e (3) magnitude da razão de interação rocha/água ou rocha/fluidos durante os eventos pós-deposicionais (Brand e Veizer, 1980a,b; Veizer, 1983; Banner e Hanson, 1990, Kaufman et al., 1991). Estas variações, geralmente acompanhadas por mudanças geoquímicas, permitem diferenciar processos afetando os carbonatos desde sua precipitação ate o metamorfismo inclusive (Shieh e Taylor 1969, Dunn e Valley,1992 , Kitchen e Valley, 1995, Valey 2001, Evans, 2002). Estas conseqüentemente permitem também precisar e avaliar a confiabilidade dos registros ou assinaturas isotópicas com o objetivo de evitar determinações quimioestratigráficas errôneas.

De especial interesse nesta dissertação é a utilização de técnicas quimioestratigráficas de isótopos de oxigênio, carbono e estrôncio na caracterização de seqüências carbonáticas que sofreram metamorfismo (mármores). Com esta finalidade, uma avaliação da confiabilidade desta técnica foi realizada baseada em análise das seqüências de mármores do Complexo São Caetano, na Zona Transversal da Província Borborema, nordeste Brasileiro.

Sob esta perspectiva, se darão a conhecer os resultados da caracterização quimioestratigráfica de C, O e Sr dos mármores e se apresentaram algumas considerações acerca das condições geoquímicas da água do mar a partir da qual os protólitos destes se precipitaram. Adicionalmente, se propõe uma idade de sedimentação para os protólitos dos mármores e faz-se algumas considerações acerca de possíveis causas que levaram a mudanças na composição isotótopica da água do mar durante a sedimentação. Alterações no registro geoquímico dos mármores serão avaliadas igualmente e as causas que afetaram as seqüências determinadas, com a finalidade de mostrar como processos metamórficos afetaram a assinatura isotópica original dos carbonatos. Finalmente, uma metodologia é proposta para o trabalho quimioestratigráfico em seqüências de mármores, a qual inclui análise petrográfica e de catoluminescencia dos mármores, análises isotópicas de carbono em calcita e grafita e analise de elementos maiores e menores em carbonatos.

É importante ressaltar que esta versão impressa de dissertação de mestrado, devido à sua forma, seguindo as normas do programa de pós-graduação em Geociências da Universidade Federal de Pernambuco, não inclui capítulos como nas versões tradicionalmente submetidas, mas inclui os artigos nos quais são descritos os métodos e resultados das pesquisas realizadas nos mármores do Complexo São Caetano. O primeiro artigo, submetido aos Anais da Academia Brasileira de Ciências (2004) trata sobre as características quimioestratigráficas dos mármores estudados e implicações regionais e globais deste registro. No segundo artigo, submetido a Chemical Geology, Elsevier (2004) uma avaliação das técnicas quimioestratigráficas em mármores é feita, incluindo análise de possíveis causas de alteração do registro isotópico e caracterizarão das condições sob as quais a alteração aconteceu.

OBJETIVOS

Objetivos gerais

1. Caracterizar quimioestratigráficamente os mármores do Complexo São Caetano, nos municípios Flores e Afogados da Ingazeira, Pernambuco, com a finalidade de determinar a idade de deposição do seu protólito sedimentar e investigar as causas de mudanças isotópicas na água do mar da qual as seqüências carbonáticas originais se depositaram.
2. Determinar as possíveis causas de alteração das assinaturas isotópicas de C e Sr nos mármores do Complexo São Caetano e investigar se estas refletem aquela de seu protólito sedimentar.
3. Determinar temperaturas de pico de metamorfismo.
4. Propor um método multivariado para determinar alterações pós-deposicionais da composição isotópica de mármores.
5. Propor um modelo de evolução para os protólitos dos mármores estudados e em geral para o Complexo São Caetano.

Objetivos específicos

1. Aplicar a sistemática de isótopos estáveis de C, O e Sr na caracterização de carbonatos.
2. Investigar variações da assinatura isotópica (C e Sr) original dos carbonatos a partir de caracterizações petrográficas e de catodoluminescência dos mármores, determinações de composições isotópicas dos carbonatos e grafitas associadas, e caracterização geoquímica de elementos maiores e menores dos mármores.
3. Aplicar o paleotermómetro calcita-grafita coexistentes, a partir de determinações da composição isotópica de carbono nos dois minerais.

C- and Sr-Isotope Atratigraphy of the São Caetano Complex, Northeastern Brazil: A contribution to the Study of the Meso-Neoproterozoic Seawater Geochemistry

Autores: Juan C.S. Tamayo, Alcides N. Sial, Valderez P. Ferreira, Márcio M.Pimentel

Dear Dr. Tamayo

On behalf of Lucia Mendonça Previato, Ph.D., Editor-in-Chiefof the Anais da Academia Brasileira de Ciências, I hereby inform that the manuscript mentioned above, submitted for publication in the Anais da Academia Brasileira de Ciências was analyzed by two referees. It might be accepted for publication after the modifications in accordance to their comments, which are being mailed to you today.

Sincerely,

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C- AND Sr- ISOTOPE STRATIGRAPHY OF THE SÃO CAETANO COMPLEX, NORTHEASTERN BRAZIL: A CONTRIBUTION TO THE STUDY OF THE MESO-NEOPROTEROZOIC SEAWATER GEOCHEMISTRY

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ABSTRACT

C-isotope and $^{87}Sr/^{86}Sr$ values for five carbonate successions from the São Caetano Complex, northeastern Brazil, were used to constrain their depositional age and to determine large variations in the C- and Sr- isotopic composition of seawater under the framework of global tectonic events. Three C-isotope stages were identified from base to top in a composed chemostratigraphic section: (1) stage in which $\delta^{13}C$ values vary from +2 to +3.7$‰_{PDB}$ and average 3$‰_{PDB}$, (2) stage with $\delta^{13}C$ values displaying stronger oscillations (from -2‰ to +3$‰_{PDB}$), and (3) stage with an isotopic plateau with values around +3.7$‰_{PDB}$. Constant $^{87}Sr/^{86}Sr$ values (~0.70600) characterize C-isotope stage 1, whereas slightly fluctuating values (from 0.70600 to 0.70700) characterize C-isotope stage 2. Finally, $^{87}Sr/^{86}Sr$ values averaging 0.70600 characterize C-isotope stage 3.

The C- and Sr- chemostratigraphic pathways permit to state: (a) the C- and Sr-isotope secular curves registered primary fluctuations of the isotope composition of seawater during late Mesoproterozoic - early Neoproterozoic transition in the Borborema Province, and (b) onset of the Cariris Velhos/Greenville cycle, widespread oceanic rifting, continental magmatic arc formation and onset of the agglutination of Rodinia supercontinent, mostly controlled the C- and Sr-isotope composition of seawater during the C-isotope stages 1, 2 and 3.

1. INTRODUCTION

Well-constrained C- and Sr-isotope chemostratigraphic data for Proterozoic limestone sequences have been used to detect changes in the geochemical composition of ancient seawater and their possible causes (Jacobsen and Kaufman 1999, Bartley et al. 2001, Lindsay and Brasier 2002). Changes in the C- and Sr-composition of the Proterozoic seawater result from the net interaction of several endogenic and exogenic mechanisms, among which tectonic activity, biologic radiations and amazing climatic changes are of remarkable importance (Melezhik et al. 1997, Brasier and Lindsay 1998, Hoffman and Schrag 2002, Bekker et al. 2003).

The Mesoproterozoic - early Neoproterozoic chemostratigraphic record has been a topic of continuous discrepancies among geologists given that the lack of well-preserved stratigraphic sections has not permitted the achievement of a well-constrained geochemical database. Few works (e.g Knoll et al. 1995, Hall and Veizer 1996, Frank et al. 1997, 2003, Kah et al. 1999, 2001, Santos et al. 2000, Bartley et al. 2001, Azmy et al. 2001, Maheshwari et al. 2002, Bartley and Kah 2003) have supplied reliable chemostratigraphic information for the construction of well-constrained C- and Sr-isotope secular variation curves. Therefore, establishing factors that affected the seawater geochemistry during this time span has remained difficult. Based on the available data, it has been proposed that the early Mesoproterozoic C- and Sr- isotope composition of seawater remained in an apparent long-lasting steady state (Buick et al. 1995, Brasier and Lindsay 1998), while the middle-late Mesoproterozoic - early Neoproterozoic composition of seawater seems to have registered stronger perturbations in the geochemical cycles as a result of miscellaneous factors (Brasier and Lindsay 1998, Kah et al. 1999, Bartley et al. 2000, 2001, Bartley and Kah 2003, Frank et al. 1997, 2003).

The São Caetano Complex (SCC) marble sequences, located in the Transversal Domain of the Borborema Structural Province (BSP), northeastern Brazil (Fig. 1), is a good candidate to unravel the above mentioned chemostratigraphic problems, although its sedimentation and metamorphism ages have been poorly constrained. This work aims at: (1) indirectly constrain the depositional age of the SCC, by comparing its C and Sr-isotope chemostratigraphic curves with previously calibrated ones from other sequences worldwide, (2) enhance the global C- and Sr-isotope stratigraphy database for the late Mesoproterozoic - early Neoproterozoic time span and (3) contribute to explain on how major tectonic events produced main C- and Sr- isotope perturbations in the ocean water geochemistry during this period of the Earth's history. Finally, since our isotopic database published in this work was obtained from marble sequences (amphibolite facies), it is also aimed to assess how metamorphism may have affected the original C- and Sr- isotope composition of SCC carbonate sequences.

2. GEOLOGIC SETTING AND AGE

The São Caetano Complex (SCC) is located in the Alto Pajeú Terrane (APT), Transversal Domain of the Borborema structural province (BSP), northeastern Brazil (Fig. 1). It is a metavolcano-sedimentary sequence characterized by garnet-biotite paragneiss, quartzite, marble, metapelite, metagraywacke, metadacite, metarhyolite, and metabasalt, metamorphosed in the amphibolite-facies during late Neoproterozoic (0.75-0.5 Ga.; Brito Neves et al. 2000).

FIGURE 1

This complex is associated to metavolcanic sequences and MORB mafic-ultramafic suites (e.g Riacho-Gravata belt and Serrote das Pedras Pretas complex), which are interpreted as part of a mid-oceanic rift sequence developed at ~1.05 Ga (Van Schmus et al. 1995), and intruded by early and middle Neoproterozoic plutons (Brito Neves et al. 2000 and references therein). The SCC is also associated to some marine Neoproterozoic metasedimentary sequences (Cachoeirinha Complex), but field relationships between them are not conclusive.

No agreement on the stratigraphic position of the SCC has been reached thus far. The lack of high-resolution stratigraphic information has made its temporal characterization difficult, leading to several stratigraphic proposals. Despite the SCC has been strongly affected by regional shear zones and has been extensively intruded by Neoproterozoic plutonic suites during the Cariris Velhos cycle (0.96-0.95 Ga; Kozuch unpublished results), and Pan-African/Brasiliano orogeny (Brito Neves et al. 2000), the marble successions studied here have thicknesses and extensions that can assure their regional character.

The studied SCC marble successions are mainly calcitic and contain silicate mineral assemblages typical of amphibolite facies (diopside-tremolite-muscovite-garnet). These marbles contain considerable amounts of graphite, which are disposed in layers and present different cyclic pathways (Fig. 2). They are interbedded with siliciclastic successions, and their thickness diminishes upward section. In spite of strong folding and shearing to which the SCC has undergone, the marble sequences seem to have preserved original stratigraphic polarity. This is corroborated by the presence of non-mimetic chemostratigraphic pathways as discussed below.

FIGURE 2

The age of the SCC is poorly constrained. The oldest age (> 1.3 Ga.) ascribed to this complex was inferred from sedimentary zircons of Archean to Late Mesoproterozoic collected from siliciclastic successions in the uppermost portion of the SCC (Brito Neves et al. unpublished results). The youngest age for this complex was assumed from a 0.96 Ga (U-Pb) age determined for a granodioritic-biotite orthogneiss that intruded the siliciclastic successions overlying the studied marbles (Kozuch unpublished results).

3. MATERIALS AND METHODS

Marble samples were thin-sectioned in order to determine their petrographic characteristics and to evaluate whether silicate phases or graphite had some effect on the isotopic record. Determinations of minor and major elements were performed using X-Ray fluorescence to support the petrographic analyses and to further evaluate post-depositional alterations. These analyses were performed in a Rigaku RIX 3000 XRF unit, equipped with a Rh tube, at the XRF laboratory, Department of Geology, Federal University of Pernambuco. Analyses of major and minor elements are reported in parts per million (ppm).

For C- and O-isotope analyses, powdered carbonate samples were reacted with 100% orthophosphoric acid during 12 hours at 25°C. The CO_2 released from this reaction was extracted in a high-vacuum extraction line by using cryogenic cleaning according to the method proposed by Craig (1957). The CO_2 samples were analyzed for C and O- isotopes in a multi-collector double-inlet gas source mass spectrometer (Sira II), at the Stable Isotope Laboratory (LABISE), Department of Geology, Federal University of Pernambuco. The isotopic composition were contrasted against the in-house standard Borborema Skarn Calcite (BSC), which calibrated against the NBS-18, NBS-19 and NBS-20 standards, shows an isotopic composition of $\delta^{18}O = -1.28 \pm 0.04‰_{PDB}$ and $\delta^{13}C = -8.58 \pm 0.02‰_{PDB}$. Results are reported in the international δ‰ (*delta permil*) notation respect to the PDB scale.

For determination of the Sr-isotopic composition, 5 mg of powdered carbonate sample were dissolved in 0.5M ultraclean acetic acid for leaching, and centrifuged to obtain purified Sr. Rb and Sr were separated from the leached solutions by standard ion-exchange techniques. Following, 500 to 1000 ng of purified Sr were loaded onto Ta filament, along with 1μm H_3PO_4, for TIMS analysis, in a seven collector Mat 262 instrument at the Geochronology Laboratory, Institute of Geosciences, University of Brasilia.

4. CONSTRAINING POST-DEPOSITIONAL ISOTOPIC ALTERATION

C- and Sr-isotope composition of marine carbonate materials has been successfully used to determine changes in the geochemistry of ancient oceans (Veizer and Hoefs 1976). Nevertheless, diagenesis and/or metamorphism have been considered as potential processes capable to cause post-depositional alteration of the original C- and Sr-isotope signatures. When submitted to either one of these processes, carbonates undergo textural, mineralogical and geochemical alterations, favored by (1) presence of C- and/or Sr- bearing minerals, (2) presence of intergranular or intercrystalline fluids, whose C- and Sr-isotope compositions differ from that of the carbonate, (3) abundance of primary elements into the carbonate lattice, and (4) extent of the water-rock interaction during precipitation, deposition and post-depositional processes (Brand and Veizer 1980 a, b, Banner and Hanson 1990, Kaufman et al. 1991).

The presence of silicate minerals and/or graphite has been considered as a potential factor capable of generating post-depositional change of the original C-isotope signature of carbonates, leading to depletions of their $\delta^{13}C$ values (Shieh and Taylor 1969). It has been also determined that the presence of silicate minerals affect the original $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ signatures as well (Chacko et al. 1991, Valley and O'Neil 1981, Valley 2001). Additionally, it has been established that paired depletions in $\delta^{18}O$ and $\delta^{13}C$ chemostratigraphic trends can be expected during post-depositional isotopic alteration.

In order to determine post-depositional alteration and discriminate altered samples, which can yield erratic chemostratigraphic pathways, a petrographic characterization of the carbonates samples was performed. In general, studied marbles present coarse-grained calcite (0.8 to 4 mm). Graphite contents vary between 0 and 8% and present a general coarsening up tendency (grain sizes from 0.1 to 2 mm). It is either randomly disposed in layers or in disseminated form. Silicate phases (quartz, muscovite, tremolite, and diopside) are no representative (Fig. 3). No dissolution or exsolution textures were found, except when calcite crystals are in contact with graphite.

FIGURE 3

Given to the presence of graphite and silicate minerals in the SCC marbles, $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ data were cross-plotted and examined against some other geochemical tracers to determine possible post-depositional modifications (Fig. 4). Besides, the $\delta^{13}C$ and $\delta^{18}O$ secular variation curves were contrasted against the presence of graphite and silicate minerals (Fig. 5,6). No paired depletions were identified and no relationship was found between presence of silicate minerals and anomalously depleted isotopic values (Fig. 6). Depletions in the $\delta^{13}C$ occur independently of the presence and variations in the percentage of silicate minerals and an opposite behavior was observed when comparing the $\delta^{13}C$ curve with the graphite content one. In general depletions on the $\delta^{13}C$ values accompany increases in graphite content and size, in sectors where the graphite occurs accumulated in layers (Fig. 5,6).

Other geochemical parameters were used to further investigate post-depositional alterations, following methods proposed by Derry et al. (1992), Kaufman et al. (1991, 1993) and Kaufman and Knoll (1995) (Table 1, Fig. 4). Sr contents varying from 552 to 2487 ppm and averaging 1500 ppm, as well as Mn/Sr ratios varying from 0.006 to 0.140, and Rb/Sr ratios between 0 and 0.005, were found in the SCC marbles. These values perfectly meet the unaltered ratio ranges proposed by Bartley et al. (2001) for unaltered limestone sequences in Siberia, and are in close agreement with those lying in the field of unaltered samples (Sr contents > 1000 ppm) proposed by Brand and Veizer (1980a). Additionally, most of the obtained Sr values fall within the unaltered range (1100 and 1400 ppm) that Kah et al. (1999, 2001) proposed as representative of pristine seawater composition in Meso-Neoproterozoic limestone sequences located in Canada.

TABLE 1

FIGURE 4

In summary, the elemental composition of most of the analyzed SCC marble samples lies in the fields of unaltered rocks (Fig. 4). This indicates that the original composition of the limestone sequences has been preserved and effectively buffered during early diagenesis by ocean diagenetic fluids, preventing post-depositional alteration and allowing to low water-rock interaction (W-R) during diagenesis and metamorphism. However, few post-depositional modifications of the C-isotope record were found for samples with high graphite content. Carbonate samples with anomalously negative δ^{13}C are thought to be a result of possible post-depositional alteration due to graphite derived CO_2 /CH_4 - calcite fractionation during diffusion. This processes, which have been reported by several authors (e.g. Dunn and Valley 1992, Kitchen and Valley 1995, Satish-Kumar et al. 2002), would have not effectively altered the whole marble sequence due to the low W-R interaction proposed above. Nonetheless, more analyses and evaluation are needed to further constrain this process.

5. CHEMOSTRATIGRAPHY

5.1 *C-isotope chemostratigraphy*

About 120 samples from five continuous marble stratigraphic sections near Flores Town (Pedra de Cal, Santa Rosa, Rodiador, Malutagem localities) and near Sitio dos Nunes town, Pernambuco, were analyzed for C- and O- isotopes (Fig. 1).

The thicker and most complete stratigraphic section (Pedra de Cal locality) consists of 44 samples that correspond to nearly 110 m of continuous profile (Fig. 5a). The sequence starts with a very oscillating $\delta^{13}C$ pathway, which fluctuates between +2‰$_{PDB}$ and +3.6‰$_{PDB}$ and presents some depletion to values around 1‰$_{PDB}$. Upsection, those values remain almost constant, averaging +2.3‰$_{PDB}$, then decrease to values as low as -2.2‰$_{PDB}$ and finally stabilize around -1.5 ‰$_{PDB}$. Some positive shifts (of no more than 0.5‰$_{PDB}$) are also noticeable. A positive excursion, from 0 to +1.8‰$_{PDB}$, characterizes the upper portion of the section just before falling to values around 0 and -1‰$_{PDB}$ in its uppermost portion.

FIGURE 5

The Malutagem (Fig. 5b) and Sitio dos Nunes sections (Fig. 5c) display predominantly negative $\delta^{13}C$ values. Both sections start with oscillating values, in which shifts from -2.6‰$_{PDB}$ to ~+1‰$_{PDB}$ are identified. This pathway is interrupted by a very pronounced enrichment from -1.5 to +2.5‰$_{PDB}$, which finally decreases to values near -2‰$_{PDB}$ upsection .

The Santa Rosa (Fig. 5d) and Rodiador (Fig. 5e) sections display the most positive $\delta^{13}C$ values in this study. Both sections start with negative $\delta^{13}C$ values, -1.8‰$_{PDB}$ and -1.4‰$_{PDB}$ respectively, which then increase upsection reaching values as high as +3.7‰$_{PDB.}$ In the Rodiador section those positive values sporadically decrease to values near -1.8‰$_{PDB}$, which were interpreted as the result of post-depositional alteration; whereas in the Santa Rosa section, positive values (+2.7‰$_{PDB}$) are preserved and no shift towards negative values has been recorded.

Samples with possible post-depositional alteration were discarded (see previous section) and the $\delta^{13}C$ chemostratigraphic pathways were used to correlate the stratigraphic sections and to construct a composite C-isotope variation curve (Fig. 6). The correlation between stratigraphic sections was performed contrasting C-isotope anomalies. Three C-isotope stages were identified: (a) C-isotope stage 1, mostly characterized by the presence of positive $\delta^{13}C$ values (from +2.3 to +3.6‰$_{PDB}$); (b) C-isotope stage 2, characterized by a very fluctuating $\delta^{13}C$ pathway, which starts with a large negative excursion (from ~+2 to ~-2‰$_{PDB}$), then increase to values ~+2.4‰$_{PDB}$, to subsequently shift back to values near -2‰$_{PDB}$ and to finally increase towards values around 3‰$_{PDB}$; and (c) C-isotope stage 3 that displays a noticeable and constant increase, from ~-2‰$_{PDB}$ to ~+3.7‰$_{PDB}$.

FIGURE 6

The composite chemostratigraphic trends are accompanied by changes in the chemical and mineralogical composition of carbonates. An increasing, upward tendency in the Mg/Ca ratio, accompanied by the presence of few silicate phases (predominantly quartz, muscovite and tremolite) and variable amounts of graphite, characterizes the C-isotope stage 1. On the other hand, low graphite contents and slightly higher amounts of silicate minerals (quartz and tremolite) characterize C-isotope stage 2, in which a mimetic behavior between the Mg/Ca ratios and the C-isotope values is observed. Finally, C-isotope stage 3 contains low amounts of graphite and silicate minerals and presents an increasing tendency in the Mg/Ca ratios, which is less pronounced in magnitude that those observed in C-isotope stage 2 (Fig. 6).

In summary, changes in C-isotope chemostratigraphic trends keep a co-variation with Mg/Ca ratios and amount of graphite (Fig 6). As exposed above, shifts in the C-isotope composition of carbonates coincide with changes in the amount of graphite (Figs. 4, 5) and its distribution in outcrop (Fig. 2). Low amounts of graphite, disposed in layers, characterize the C-Isotope stage 1, whereas variable amounts of graphite, disposed in layers and some times disseminated, are commonly found associated to C-isotope stage 2. Finally, variable amounts of graphite, although less pronounced than those observed in C-isotope stage 2, are found in most of cases disposed in layers in the stratigraphic interval corresponding to the C-isotope stage 3.

5.2 *Sr- isotope stratigraphy*

A composite $^{87}Sr/^{86}Sr$ curve was constructed based on the well-constrained C-Isotope composite chemostratigraphic curve (Fig. 6). $^{87}Sr/^{86}Sr$ values averaging 0.706 where found in the lower portion of the sequence, characterizing the C-isotope stage 1. Values increase to ~0.707 and then fall again, up section, to values near 0.706 in the stratigraphic interval corresponding to the C-isotope stage 2, to finally shift to values ~0.707. In the uppermost portion of the sequence and coinciding with the C-isotope stage 3, values decrease to ~0.706, remaining constant through the upper-most portion of the composite chemostratigraphic curve.

6. DISCUSSION

6.1 Regional implications of the São Caetano Complex C and Sr isotope composition

C- and Sr-isotope composition of carbonate sequences has been successfully used to correlate marine carbonate sequences worldwide and to indirectly constrain their depositional age (Kah et al. 1999, Bartley et al. 2001, among others). The effectiveness of this approach has not only been demonstrated for limestone sequences, but also on marble successions, in which the lack of fossils and other geochronologic indicators make age determinations rather difficult (Kaufman et al. 1991).

The $\delta^{13}C$ secular variation pathways encountered in the SCC marbles seem to closely match with those encountered in Meso-Neoproterozoic carbonate sections in Canada and Siberia (Fig. 7) (Knoll et al. 1995, Kah et al. 1999, Bartley et al. 2001). For instance, carbonate sequences from Siberia (Bartley et al. 2001) and Canada (Kah et al. 1999) present mostly positive $\delta^{13}C$ values (~+4‰$_{PDB}$), which are interrupted by a large depletion towards negative values(-2.7‰$_{PDB}$); the latter separated by a large positive excursion of near ~5‰$_{PDB}$ (from -2.4 to ~+2.4‰$_{PDB}$) (Fig. 7). According to Bartley et al. (2001) such a positive excursion (-2.4 to +2.4‰$_{PDB}$) marks the Meso-Neoproterozoic passage (~1 Ga). On the other hand, the age of the positive isotopic plateau (3-4‰$_{PDB}$) preceding the above mentioned positive excursion was constrained based on a Pb-Pb isochron for carbonates from Siberia, which yield an age of 1.03 Ga (Ovchinnikova et al. 1995). Additional age data, based on isotopic analyses of glauconite-illite series minerals, provided an age of near 1.17 Ga for the stratigraphic levels presenting this isotopic plateau in the Kerpyl Group, Siberia (Bartley et al. 2001).

FIGURE 7

Bartley et al. (2001) reported $^{87}Sr/^{86}Sr$ data averaging 0.706 from some middle Riphean sucessions in Siberia (Turukhansk Uplift, Sukhaya Tunguska Formation) and values between 0.706 and 0.7065 from their late Riphean counterparts. These data supplemented the data obtained by Kah et al. (2001), who reported values between 0.7052 and 0.706 from Mesoproterozoic carbonates of the Bylot Supergroup in Canada, as well as from gypsum successions of the Society Cliffs Formation in Canada. Nevertheless, Gorokhov et al. (1995) reported increasing

^{87}Sr/^{86}Sr ratios, from 0.706 to 0.7065, obtained in middle-late Riphean (Meso-Neoproterozoic transition) successions in Siberia.

The ^{87}Sr/^{86}Sr values reported in the literature for the Mesoproterozoic – Neoproterozoic transition are quite similar to those for the SCC marble sequences (Fig. 7). Although Bartley et al. (2001) proposed that ^{87}Sr/^{86}Sr values around 0.705 characterize the middle-upper Riphean transition, values around 0.707 found for SCC marbles are quite similar to those reported by Gorokhov et al. (1995) for the same time span. However, similar values from the Turukhansk Uplift (Siberia) were considered by Bartley et al. (2001) as representing post-depositional alteration.

On the basis of the similarities between the C- and Sr-isotope chemostraigraphic pathways encountered in the above-mentioned carbonate sequences and those herein reported from the SCC, a sedimentation spanning from 1.1 to ~0.97 Ga is proposed. This suggests that oceanic conditions likely dominated part of the Transversal Domain of the Borborema Structural Province during the Meso-Neoproterozoic boundary and consequently, that the Transversal Domain remained as an open oceanic basin during that time span. This implies that the proposed landmasses collisional processes associated to the agglutination of Rodinia supercontinent (Brito Neves et al. 2000), would have not taken place before 0.97 Ga in the Transversal Domain. The same conclusion has been recently reached by Kröner and Cordani (2003) who envisaged the possibility of a small and narrow oceanic basin in the Transversal Domain, during a period of continental expansion and rifting around 1.0 Ga.

6.2 Global Implications of the late Mesoproterozoic - early Neoproterozoic C and Sr-Isotope record

Since changes in the C- and Sr-isotope composition of seawater have been ascribed to miscellaneous processes, a brief discussion about the factors that can eventually affect such an isotopic composition will be addressed before discussing the late Meso- early Neoproterozoic record.

Oscillatory δ^{13}C pathways encountered in carbonate sequences worldwide have been attributed, in the long term, to periods of high tectonic activity during which inputs and outputs of the available C_{org} resulted in changes in the C-isotope composition of seawater respectively (Derry et al. 1992, Lindsay and Brasier 2002, Bekker et al. 2003). For instance, enriched δ^{13}C values have been attributed to periods of high tectonic activity during which enhanced C_{org} burial causes high levels of oxygenation levels in ocean and atmosphere, as well as high biologic diversification events (Des Marais 1997). These values are also expected during periods of high C_{org} sequestration during widespread subduction of C_{org}-rich sedimentary slabs and during widespread oceanic closure (Lindsay and Brasier 2000, 2002, Bekker et al. 2003). Alternatively, it has also been proposed that short lasting phenomena such as upwelling, relative sea level changes, ocean water stratiphication, among other, can also generate fluctuating, environment dependant $\delta^{13}C$ pathways in the sedimentary record as observed in Phanerozoic sedimentary succession (Mitchell et al. 1996, Scholle and Arthur 1980). Oppositely, low $\delta^{13}C$ values are associated to periods of stable tectonics, in which low C_{org} burial contribute to the oxidation and incorporation of the available crustal ^{12}C-rich organic material being incorporated into the ocean system (Des Marais 1994, Kah et al. 1999, Bartley et al. 2001). Depleted $\delta^{13}C$ values can be also expected during periods of oceanic rifting and spreading, as well as during the occurrence of mantle superplumes, in which ^{13}C-depleted volcanic CO_2 is released into the ocean water (Lindsay and Brasier 2000, 2002).

On the other hand, the Sr isotopic composition of seawater have been associated to diverse phenomena such as mid-oceanic rifting (outgassing), alteration of seafloor basalt and continental crust weathering and associated Sr isotope incorporation into the ocean via riverine discharge. Under this perspective, general agreement exists in that low $^{87}Sr/^{86}Sr$ values have been associated to mid oceanic volcanic activity (outgassing) and to alteration of seafloor basalt, whereas high $^{87}Sr/^{86}Sr$ values have been associated mostly to continental weathering (Veizer et al. 1997).

The Mesoproterozoic seems to have been a crucial period of the evolution of Earth, during which strong and global tectonic events (e.g Grenville, agglutination of supercontinent Rodinia, widespread rifting) (Hoffman 1999), large C_{org} sequestration through burial and concomitant oceanic redox conditions (Des Marais et al. 1992, Canfield 1998), carbonate saturation of ocean water (Kah et al. 2001, Bartley and Kah 2003) and biochemical ecstasy (Knoll 1992) seem to have fashioned the C-isotope composition of seawater.

Some authors (e.g. Buick et al. 1995, Knoll et al. 1995, Brasier and Lindsay 1998) have proposed that tectonic stability, biochemical ecstasy (appearance and diversification of Eukaryotes) and oceanic geochemical quiescence derived from large ocean-atmosphere equilibrium generated an almost invariant C-isotope composition of the Mesoproterozoic seawater. Other authors, in contrast, have invoked the occurrence of enhanced C_{org} matter burial, occurring during the agglutination of Rodinia, to explain secular variations in the middle Meso-early Neoproterozoic $\delta^{13}C$ record (Kah et al. 1999, Bartley et al. 2001). Such an enhancement in the C_{org} burial would have prevented ^{12}C-rich material to oxidize and thus, the concomitant incorporation of the available ^{12}C into the ocean water, generating high ocean water oxygenation levels that led to an increase in life diversification, which in turn, generated a general $\delta^{13}C$ increase in the seawater due to high ^{12}C biological consumption.

Alternatively, Bartley and Kah (2003) and Frank et al. (2000, 2003) proposed that these slightly fluctuating C-isotope pathways should have been related to large changes in the biochemical cycles and in the mass balance between the inorganic (C_{carb}) and organic (C_{org}) carbon reservoirs; which would have resulted in ^{13}C depleted-anoxic deep ocean and ^{13}C-rich shallow marine waters.

On the other hand, variation in the Mesoproterozoic Sr-isotope chemostratigraphic record has been somehow more understood than the C-isotope one, despite the scarcity of data. It has been proposed, for example, that such an increase in the seawater Sr-isotope composition (from ~0.704 to ~0.707) occurring between the early Mesoproterozoic and early Neoproterozoic seems to have occurred as a result of changes in the global tectonic activity (Veizer et al. 1992, Hall and Veizer 1996, Gorokhov et al. 1995, Bartley et al. 2001). For instance, the lowest values observed during the early Mesoproterozoic have been associated to widespread early Riphean rifting activity (Veizer et al. 1992) whereas the high radiogenic values obtained for the late Mesoproterozoic - early Neoproterozoic time span have been attributed to enhanced continental Sr inputs during the onset of the agglutination of Rodinia supercontinent and associate orogenic events (Bartley et al. 2001, Kah et al. 2001)

Based on the published C- and Sr-isotope database, on the SCC chemostratigraphic record and on other lines of evidence, it seems that the late Mesoproterozoic- early Neoproterozoic (1.1-0.97 Ga) C- and Sr-isotope composition of seawater would have been primarily controlled by tectonic activity (Fig.7). For instance, the positive $\delta^{13}C$ values (3-4‰) found in middle-middle Riphean successions worldwide (C-isotope stage 1) (Kah et al. 1999, Bartley et al. 2001) would have been controlled by a combination of global C_{org} burial and sequestration through subduction during the peak of the Grenville orogeny (~1.1 Ga.), when widespread orogenic belts and subduction zones would have extensively developed (McLelland et al. 1996). Such an orogenic peak would have also led to moderate $^{87}Sr/^{86}Sr$ values (0.7060) (Gorokhov et al. 1995) in the contemporaneous seawater as a result of large amounts of juvenile material, generated during the lower Riphean rifting event, being incorporated into the continental margins of the forming Rodinia supercontinent (Bartley et al. 2001).

In contrast, during the upper middle - late Riphean time, the occurrence of widespread rifting occurring in the São Francisco Craton (D'Agrella-Filho et al. 1990) and in between different continental landmasses (~1.05 Ga) (Kröner and Cordani 2003), including the Transversal Domain in the Borborema Province (e.g Riacho Gravata Complex; Brito Neves et al. unpublished results) as well as the apparition of several continental margin magmatic arcs (e.g Cariris Velhos, Sri Lanka) (Kröner et al. 2003, Kröner and Cordani 2003, Brito Neves et al. unpublished results) would have considerably affected the C- and Sr- seawater isotope composition (Fig. 7). The former tectonic event, would have generated the decreasing $\delta^{13}C$ trends (from +2 to -2‰) observed in unmetamorphosed sequences (Knoll et al. 1995, Kah et al. 1999, Bartley et al. 2001) and those observed in metamorphosed ones (lowermost portion of the C-isotope stage 2), as a consequence of the large addition of ^{13}C depleted CO_2 during oceanic rifting. Additionally, this phenomenon would explain the low $^{87}Sr/^{86}Sr$ values (0.705-0.706) encountered for the same time span as a result of addition of large volumes of oceanic (juvenile) crust (Fig. 7) (Gorokhov et al. 1995, Bartley et al. 2001).

The occurrence of the above mentioned continental margin magmatic arcs (1.0 Ga), in contrast, would have caused the observed $\delta^{13}C$ positive excursion (Knoll et al. 1995, Kah et al. 1999, Bartley et al. 2001) during the middle interval of the C-isotope stage 2. This short lasting and sharply positive excursion would have been the result of the extensive sequestration of C_{org}-rich materials, through burial and subduction, during a period of global sea level rise (Knoll et al. 1995, Li et al. 2003); which would have caused the C-isotope composition of seawater to fluctuate. In other words, the increasing ^{13}C enrichment, which resulted from C_{org} sequestration, would have rapidly shifted back towards the negative values observed below such a positive excursion as a result of a sea level rise. Finally, this continental margin magmatic arc and related mountain building would have invigorated the exumation of continental crust material, causing a slight increase in the $^{87}Sr/^{86}Sr$ values to 0.7070 as well (Fig. 7).

The negative $\delta^{13}C$ values (~-2‰) that characterize the middle-upper portion of the C-isotope stage 2, which then shift back towards positive values (~+3‰) in its upper most part and finally reach ~+3.7‰ in the C-isotope stage 3 characterize the early-middle Upper Riphean time and are interpreted here as the conjugation of the two following factors: (a) the continuing sequestration through subduction of ^{12}C-rich continental derived material, associated to the onset of the above mentioned continental margin magmatic arc (1.0 and 0.97 Ga.) (Kröner et al. 2003, Kröner and Cordani 2003), and (b) enhanced global sea level fall (Fig. 7).

From this panorama, it can be concluded that the C- and Sr- secular variation curves for the SCC and, in general, the late Mesoproterozoic- early Neoproterozoic C and Sr-isotope curve, seem to represent variations in the original geochemistry of seawater, which in turn would have been controlled by worldwide major tectonic events during its deposition (e.g. peak of the Grenville orogeny (1.1 Ga), oceanic rifting activity (1.05 Ga) and continental magmatic arc formation (=Cariris Velhos event; 1.0- 0.85 Ga). The same kind of mechanisms were evoked by Lindsay and Brasier (2002) to explain perturbations in the C-isotope composition of seawater during the Paleoproterozoic, period during which tectonic activity produced noticeable shifts in the seawater geochemistry after a period of apparent geochemical quiescence. Hence, major tectonic episodes must be regarded as primordial factors capable to control and modify the global C-cycle and thus the C- and Sr - isotope composition of seawater through time.

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Resumo

Valores de isótopos de C e $^{87}Sr/^{86}Sr$ de cinco seqüências de carbonatos do Complexo São Caetano, nordeste do Brasil foram usados para estimar a sua idade de deposição e relacionar variações da composição isotópica na água do mar com eventos tectônicos globais. Três estágios de variação de isótopos de carbono foram identificados de base para o topo numa seção quimioestratigráfica composta: (1) estágio em que $\delta^{13}C$ varia de +2 a +3.7‰$_{PDB}$ (media 3‰$_{PDB}$), (2) estágio no qual $\delta^{13}C$ varia consideravelmente (de -2 a +3‰$_{PDB}$) e (3) estágio apresentando valores constantes de cerca de +3.7‰$_{PDB.}$ Valores de $^{87}Sr/^{86}Sr$ ~0.70600 caraterizam o estágio isotópico 1, tornando-se mais variáveis no estágio isotópico 2 (entre ~0.70600 e ~0.70700). Finalmente, valores em torno de 0.70600 caraterizam o estagio isotópico 3.

A quimioestratigrafía de C e Sr permite concluir que: (a) as curvas de variação seculares dos carbonatos do Complexo São Caetano registram flutuações primárias na composição isotópica de C e Sr da água do mar durante a passagem Meso-Neoproterozoico na Província Borborema; (b) o ciclo orogênico Cariris velhos/Grenville, a ocorrência de rifteamento e formação de arcos magmáticos continentais, e a formação do supercontinente Rodinia, controlaram a composição isotópica de C e Sr da água do mar durante os estágios isotópicos 1, 2, 3.

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FIGURE CAPTIONS

Figure 1. Geologic map of the studied area. Numbers represent the location of the stratigraphic sections: 1.Pedra de Cal, 2. Santa Rosa, 3. Malutagem, 4. Rodiador.Tectonic terranes map are from Ferreira et al. (1998). Geologic map modified from Gomes (1999).

Figure 2. A. Marble succession presenting cyclic graphite-rich layers (Pedra de Cal section). B. Amphibolite layer interlayered with marbles in the Pedra de Cal Section. The white rectangle is 40 cm long.

Figure 3. Main petrographic characteristics of the SCC marbles. Thin sections from the Pedra de Cal (A), Malutagem (B), Rodiador (C) and Santa Rosa (D) sections. Calcite (Ca), quartz (Qz), tremolite (Tr), garnet (Gt), graphite (Gr), muscovite (Mus).

Figure 4. Cross-plots of isotopic and elemental data from all studied stratigraphic sections. Arrows indicate geochemical postdepositional alteration trends, showing that most samples fall in the unaltered fields. Geochemical trends

were used as proposed by Derry et al.(1992), Kaufman et al.(1991,1993) and Kaufman and Knoll (1995).

Figure 5. C- and O - isotope chemostratigraphic pathways for the studied marble successions. Note the inverse relationship between the $\delta^{13}C$ stratigraphic trends and variations in the graphite content. Elemental stratigraphic variations are also included.

Figure 6. C-, Sr- and O - isotope composed chemostratigraphic curve of the Sao Caetano marble successions. Roman numbers represent the C-isotope stages 1, 2 and 3 identified in this study. Perturbations in the $^{87}Sr/^{86}Sr$ secular variation curve are coincident with perturbations in the $\delta^{13}C$ secular variation curve. No correlation is observed between changes in silicate mineral assemblages and changes in the isotope curves. Special attention is drawn on the opposite behavior between the graphite content and the $\delta^{13}C$ secular variation curves. In the left most column numbers represent the studied stratigraphic sections: 1. Pedra de Cal, 2. Malutagem, 3. Sitio dos Nunes, 4. Rodiador, 5. Santa Rosa. In the right column quartz (Qz), muscovite (Mus), tremolite (Tr), diopside (Dip), garnet (Gt).

Figure 7. Chemostratigraphic C- and Sr- trends from different carbonate sequences worldwide representing the original composition of the Meso-Neoproterozoic seawater. Note the similarity between the chemostratigraphic pathways from SCC marbles and those from unmetamorphosed sequences in Siberia and Canada. Roman numbers represent C-isotope stages 1 , 2 and 3. Strong perturbations in C- and Sr- chemostratigraphic record seem to coincide with major tectonic events. (A) Offset of the Grenville orogeny, (B) Late Mesoproterozoic Rifting, (C) Cariris Velhos Orogeny, (D) Rodinia agglutination. A schematic configuration of the SCC basin is also shown. (SF) São Francisco Craton, (SL) São Luis Craton, (RG) Riacho-Gravata Complex.

SAMPLE	STRAT. SECTION	HEIGHT	δ^{13}C (PDB)	δ^{18}O (PDB)	GRAPHITE (%)	^{87}Sr/^{86}Sr	Si ppm	Ca ppm	Mn ppm	Mg ppm	Sr ppm	Rb ppm	Fe ppm
SANTROS 1	SANTA ROSA	0	-1.8	-7.2	10								
SANTROS2		0.5	-1.7	-7.4	10								
SANTROS 3		6	0.0	-7.3	10								
SANTROS 4		7	0.2	-6.8	10	0.70600							
SANTROS 5		9	0.3	-8.1	0.5		0	393780	13	6530	1966	10	1200
SANTROS 6		9.5	0.3	-7.1	0.5								
SANTROS 7		10.5	0.9	-6.0	0.5								
SANTROS 8		12	0.3	-6.6	0.5		0	390090	15	5050	2178	0	1129
SANTROS 9		17	-0.6	-5.4	0.5	0.70607							
SANTROS 10		18	0.4	-5.9	0.5								
SANTROS 11		19	1.7	-8.2	0.5								
SANTROS 12		20	2.2	-7.7	0.5								
SANTROS 13		20.5	2.4	-7.3	0.5		0	402850	10	2010	1557	0	384
SANTROS 14		21.5	2.2	-7.4	0.5								
SANTROS 15		23.5	2.4	-7.5	5								
SANTROS 16		25.5	1.7	-6.8	5								
SANTROS 17		27.5	1.4	-7.3	5								
SANTROS 18		29.3	2.4	-7.4	0.5		0	396990	10	3290	2006	0	734
SANTROS 19		30.5	2.4	-7.2	0.5								
SANTROS 20		33.5	2.7	-7.0	0.5	0.70595							
SANTROS 21		38.5	3.0	-8.3	0.5								
FLOR 1	PEDRA DE CAL	0	1.8	-6.4	0		35720	362200	57	3910	1401	10	1792
FLOR2		0.8	2.7	-6.4	0								
FLOR 3		1.6	2.0	-6.4	0								
FLOR 4		2.1	3.3	-6.2	2								
FLOR 5		3.5	3.6	-5.4	0	0.70597	0	407970	10	1980	1578	0	249
FLOR 6		4.4	3.2	-5.5	0								
FLOR 7		5.5	3.1	-6.2	0								
FLOR 8		6.5	2.0	-6.5	0								
FLOR 9		7.7	1.9	-6.1	5								
FLOR 10		8.5	2.0	-6.5	5		0	384250	78	3450	1259	0	1670
FLOR 11		10.3	1.2	-5.7	2								

FLOR 12		11.1	1.6	-6.4	2								
FLOR 13		12.1	2.9	-5.6	5								
FLOR 14		13.1	3.0	-5.6	5								
FLOR 15		15.2	3.2	-5.6	0.5		0	405780	11	2040	1572	0	309
FLOR 16		16.5	3.2	-5.1	0.5								
FLOR 17		18.85	2.4	-5.7	0.5								
FLOR 18		20.95	3.0	-5.9	0.5								
FLOR 19		23.55	2.4	-5.7	0.5								
FLOR 20		24.55	2.4	-5.7	0.5								
FLOR 21		34.55	2.2	-5.8	0.5		1044	404050	10	2070	1738	0	515
FLOR 22		37.55	2.5	-8.1	0.5								
FLOR 23		41.55	2.3	-6.5	0.5								
FLOR 24		43.55	1.2	-5.8	0.5								
FLOR 25		53.55	0.1	-4.7	8		5195	483780	24	3870	2487	0	991
FLOR 26		54.75	-0.8	-5.0	8								
FLOR 27		55.75	-0.4	-5.6	8								
FLOR 28		57.05	-1.6	-5.8	8								
FLOR 29		58.55	-2.1	-5.9	8								
FLOR 30		60.05	-1.4	-6.1	8								
FLOR 31		62.05	-1.4	-6.5	8								
FLOR 32		65.05	-1.7	-12.7	8								
FLOR 33		68.05	0.1	-7.7	8								
FLOR 34		70.05	-1.3	-13.5	8								
FLOR 35		74.05	-1.2	-11.4	5								
FLOR 36		76.05	-0.6	-8.8	5								
FLOR 37		79.05	-1.9	-11.5	5								
FLOR 38		82.05	-1.3	-7.5	5								
FLOR 39		86.05	1.7	-6.0	0	0.70597							
FLOR 40		96.05	0.1	-8.9	0								
FLOR 41		98.05	-0.7	-8.0	0								
FLOR 42		102.05	-0.7	-8.5	1								
FLOR 43		105.05	-0.9	-10.2	1								
FLOR 44		110.05	-0.8	-7.0	1								
ROD 1		0	-1.4	-8.4	13	0.70706	0	345500	21	5990	765	10	1617

ROD 2		10	3.4	-11.1	5								
ROD 3		12	3.6	-10.0	5		0	371210	80	4130	1107	10	1234
ROD 4	RODIADOR	15	3.2	-7.0	5								
ROD 5		20	3.7	-7.6	2								
ROD 6		21.5	-1.8	-13.9	10	0.70607							
ROD 7		22.5	-1.6	-10.8	10								
ROD 8		24.5	1.9	-7.6	10								
ROD 9		27	-0.0	-8.5	10		0	377500	9	22580	970	0	493
ROD 10		29	-0.9	-10.5	10								
ROD 11		31	0.1	-8.6	4								
ROD 12		33	1.5	-6.7	4		0	375130	45	3440	1464	10	1463
ROD 13		36	2.1	-6.9	4								
ROD 14		40	1.7	-6.8	4								
ROD 15		44	1.8	-7.1	4								
ROD 16		46	2.1	-7.5	3	0.70607							
ROD 17		49	2.7	-10.4	13								
ROD 18		51	2.5	-6.2	13								
ROD 19		56	0.4	-6.7	13								
ROD 20		60	-0.5	-7.5	15								
MALU 1	MALUTAGEM	0	-0.6	-8.3	2								
MALU 2		2.3	-0.9	-9.3	2								
MALU 3		3.5	-1.5	-7.0	2								
MALU 4		5	-0.6	-8.3	5								
MALU 5		6	0.2	-8.5	0.5								
MALU 6		8	-0.6	-8.3	5		0	394590	10	10370	822	0	230
MALU 7		9.5	-0.4	-9.0	5								
MALU 8		10.5	0.8	-9.2	5								
MALU 9		11	-0.4	-11.0	0.5								
MALU 10		12	2.3	-6.5	0.5								
MALU 11		12.5	2.2	-7.7	0.5								
MALU 12		13.5	2.0	-7.8	0								
MALU 13		15.5	-0.7	-6.8	8								
MALU 14		16	-0.8	-7.0	8								
MALU 15		16.5	-0.3	-6.9	8		0	400610	29	2900	2142	0	382

MALU 16		19.5	0.2	-7.4	8								
MALU 17		20.5	0.2	-7.6	9								
MALU 18		21.5	-0.5	-7.5	5								
MALU 19		24.5	-0.8	-8.1	5								
MALU 20		25	-1.7	-13.9	5								
MALU 21		26	-1.7	-13.9	5		0	366180	65	4000	2014	10	5164
MALU 22		27	-1.1	-13.8	5								
MALU 23		28	-0.8	-9.7	5								
NUNES 1	SITIO DOS NUNES	0	-2.6	-7.5	10		0	349890	79	6350	1658	22	2201
NUNES 2		1.2	-2.2	-6.0	10	0.70681							
NUNES 3		2.2	-2.3	-6.5	8								
NUNES 4		4.2	-1.4	-9.7	8								
NUNES 5		5.7	-2.1	-6.8	8								
NUNES 6		9.2	-2.2	-6.1	8		0	379950	51	10490	552	10	1757
NUNES 7		11.2	2.3	-7.5	0.5								
NUNES 8		12.7	-1.1	-6.6	8	0.70594	0	363310	38	3930	1968	0	5520
NUNES 9		14.7	-2.1	-8.5	8	0.70696	0	382460	81	6330	574	10	1939
NUNES 10		15.7	-0.9	-8.9	8								

Table 1. Geochemical analyses of representative samples of the studied marble sequences

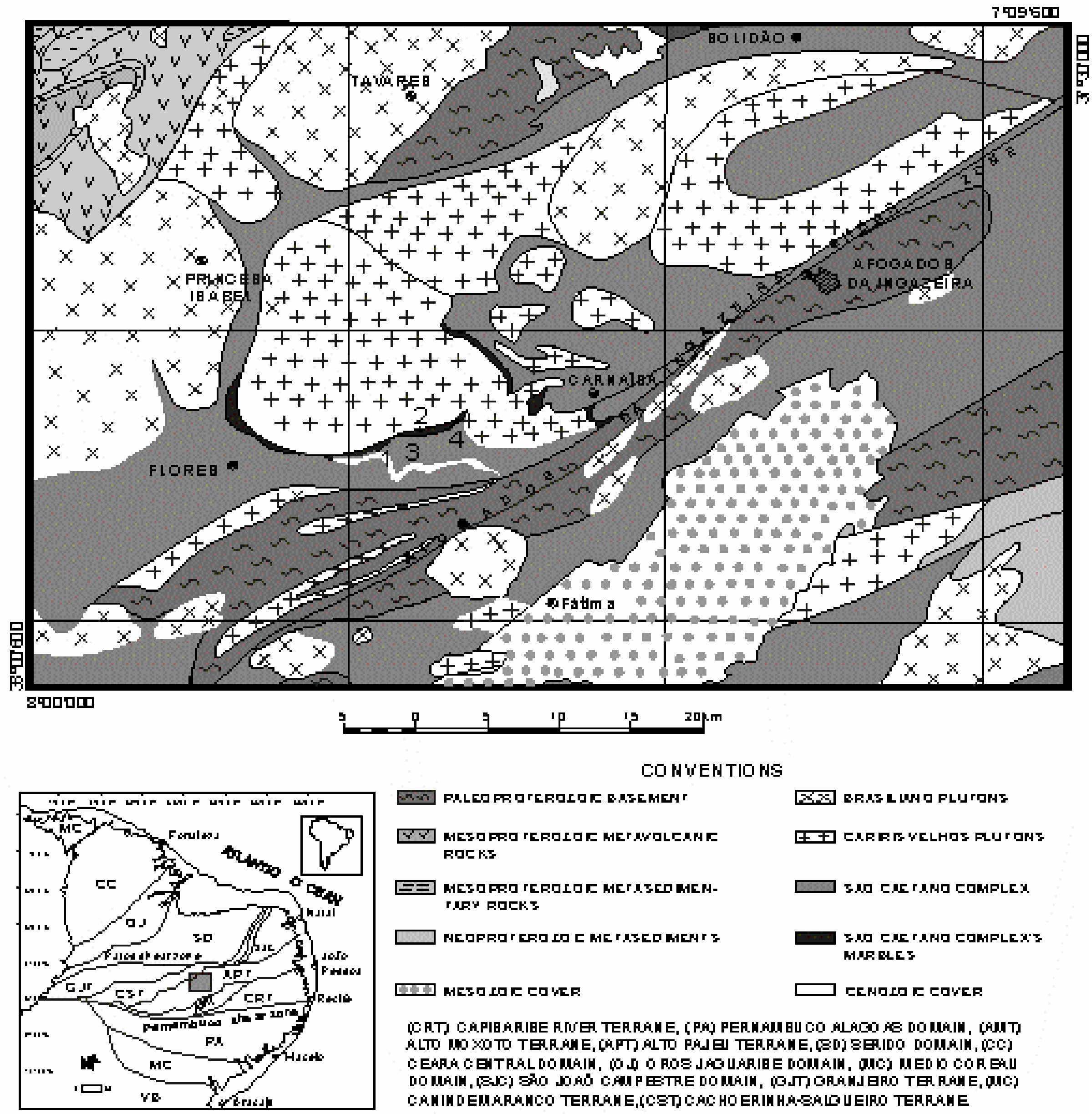
7°09'600
BOLIDÃO
TAVARES
PRINCESA ISABEL
AFOGADOS DA INGAZEIRA
CARNAÍBA
FLORES
Fátima
1
2
3
4
8°00'000
5
0
5
10
15
20km
CONVENTIONS
PALEOPROTEROZOIC BASEMENT
MESOPROTEROZOIC METAVOLCANIC ROCKS
MESOPROTEROZOIC METASEDIMENTARY ROCKS
NEOPROTEROZOIC METASEDIMENTS
MESOZOIC COVER
BRASILIANO PLUTONS
CARIRIS VELHOS PLUTONS
SÃO CAETANO COMPLEX
SÃO CAETANO COMPLEX'S MARBLES
CENOZOIC COVER
(CRT) CAPIBARIBE RIVER TERRANE, (PA) PERNAMBUCO ALAGOAS DOMAIN, (AMT) ALTO MOXOTO TERRANE, (APT) ALTO PAJEU TERRANE, (SD) SERIDO DOMAIN, (CC) CEARA CENTRAL DOMAIN, (OJ) OROS JAGUARIBE DOMAIN, (MC) MEDIO COREAU DOMAIN, (SJC) SÃO JOAÕ CAMPESTRE DOMAIN, (GJT) GRANJEIRO TERRANE, (MC) CANINDE MARANCO TERRANE, (CST) CACHOERINHA-SALGUEIRO TERRANE.
MC
CC
OJ
SD
SJC
Fortaleza
ATLANTIC OCEAN
Natal
João Pessoa
Recife
Maceió
Aracaju
Patos shear zone
Pernambuco shear zone
GJT
CST
APT
CRT
PA
MC
VB

FIGURE 1

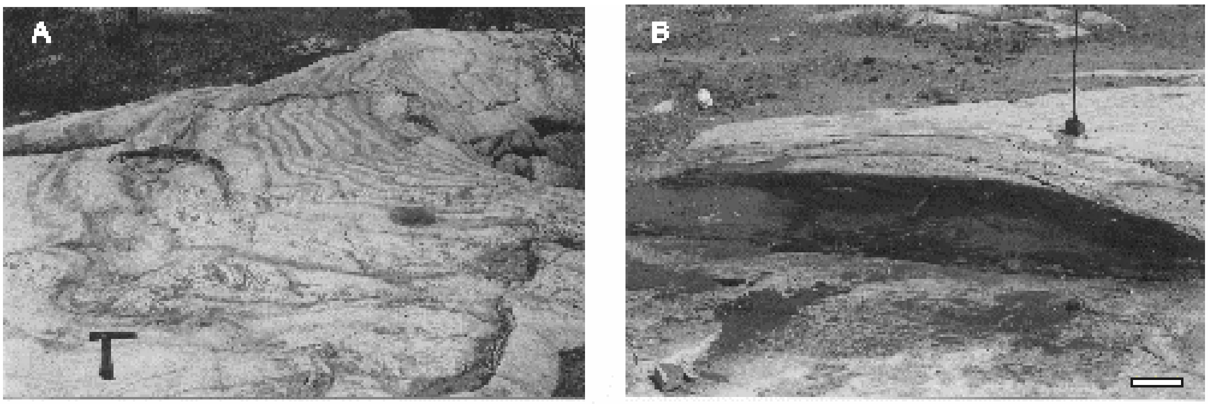

FIGURE 2

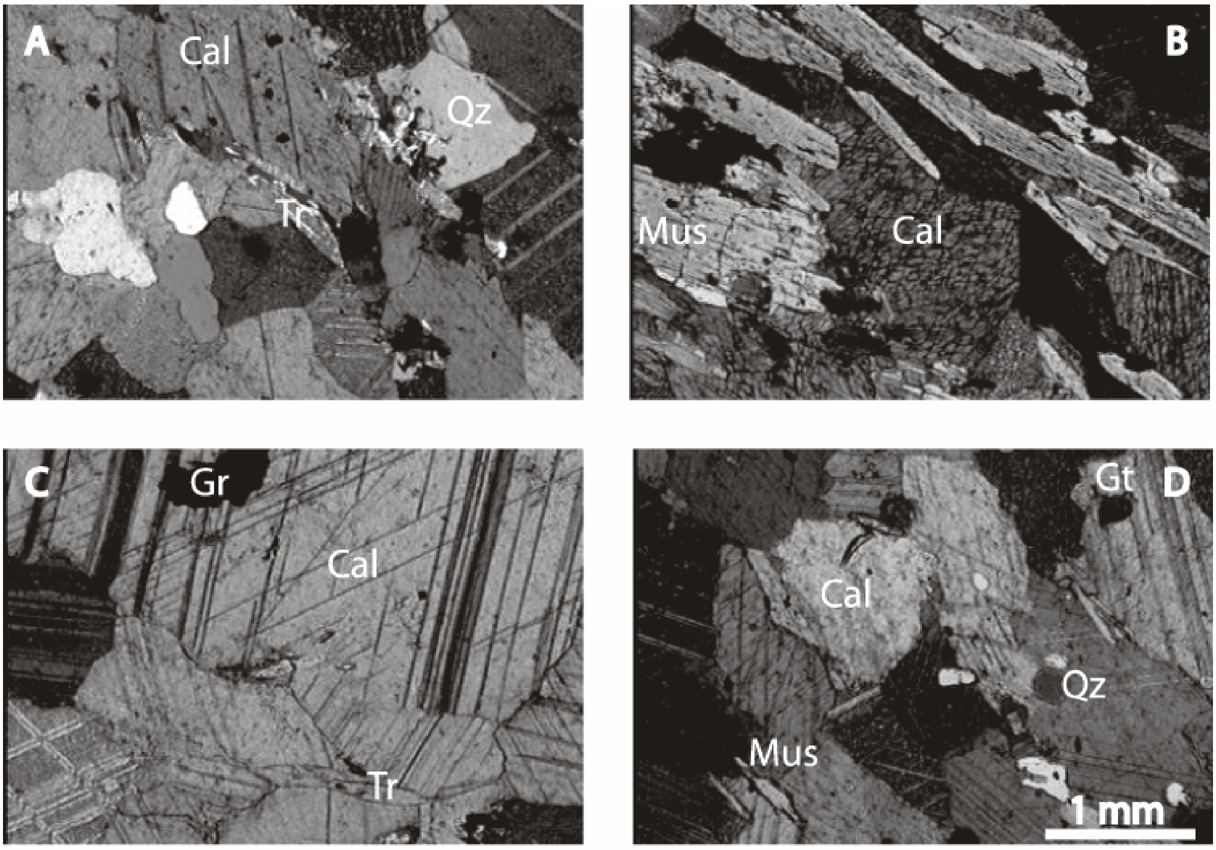

FIGURE 3

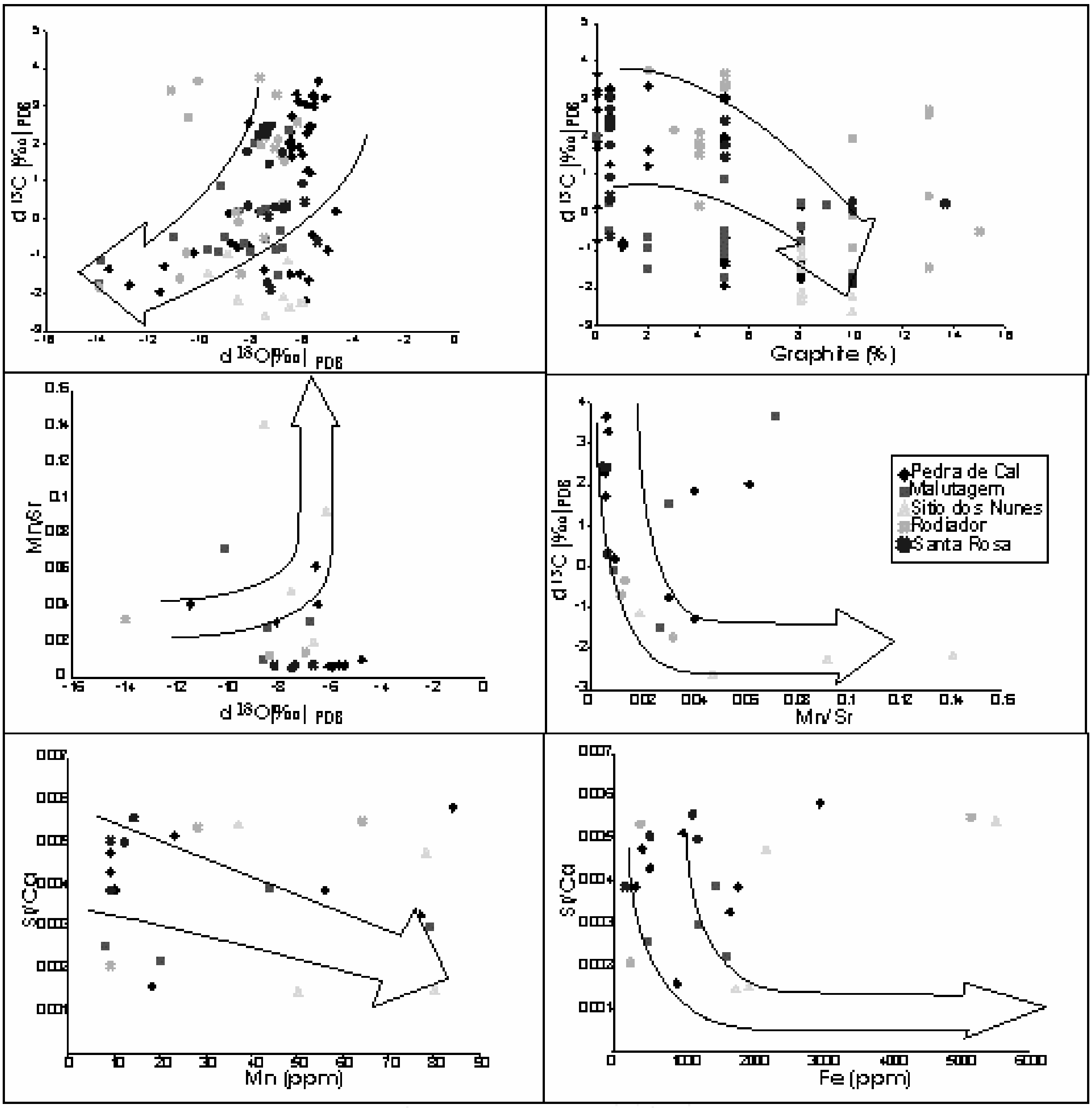
d 13C |‰| PDB
d 18O|‰| PDB
Graphite (%)
Mn/Sr
Sr/Ca
Mn (ppm)
Fe (ppm)
Pedra de Cal
Malutagem
Sitio dos Nunes
Rodiador
Santa Rosa

FIGURE 4

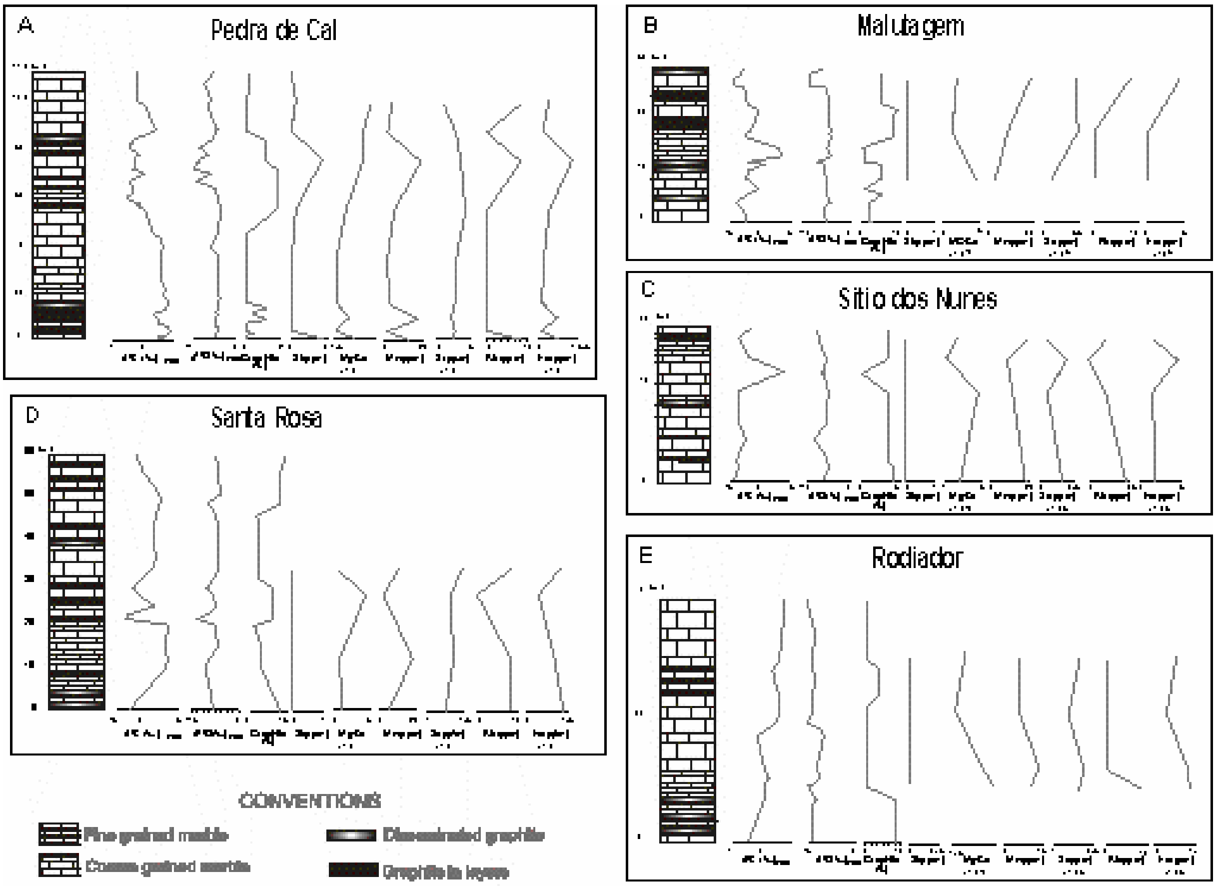
A
Pedra de Cal
B
Malutagem
C
Sitio dos Nunes
D
Santa Rosa
E
Rodiador
CONVENTIONS
Fine grained marble
Coarse grained marble
Disseminated graphite
Graphite in layers

FIGURE 5

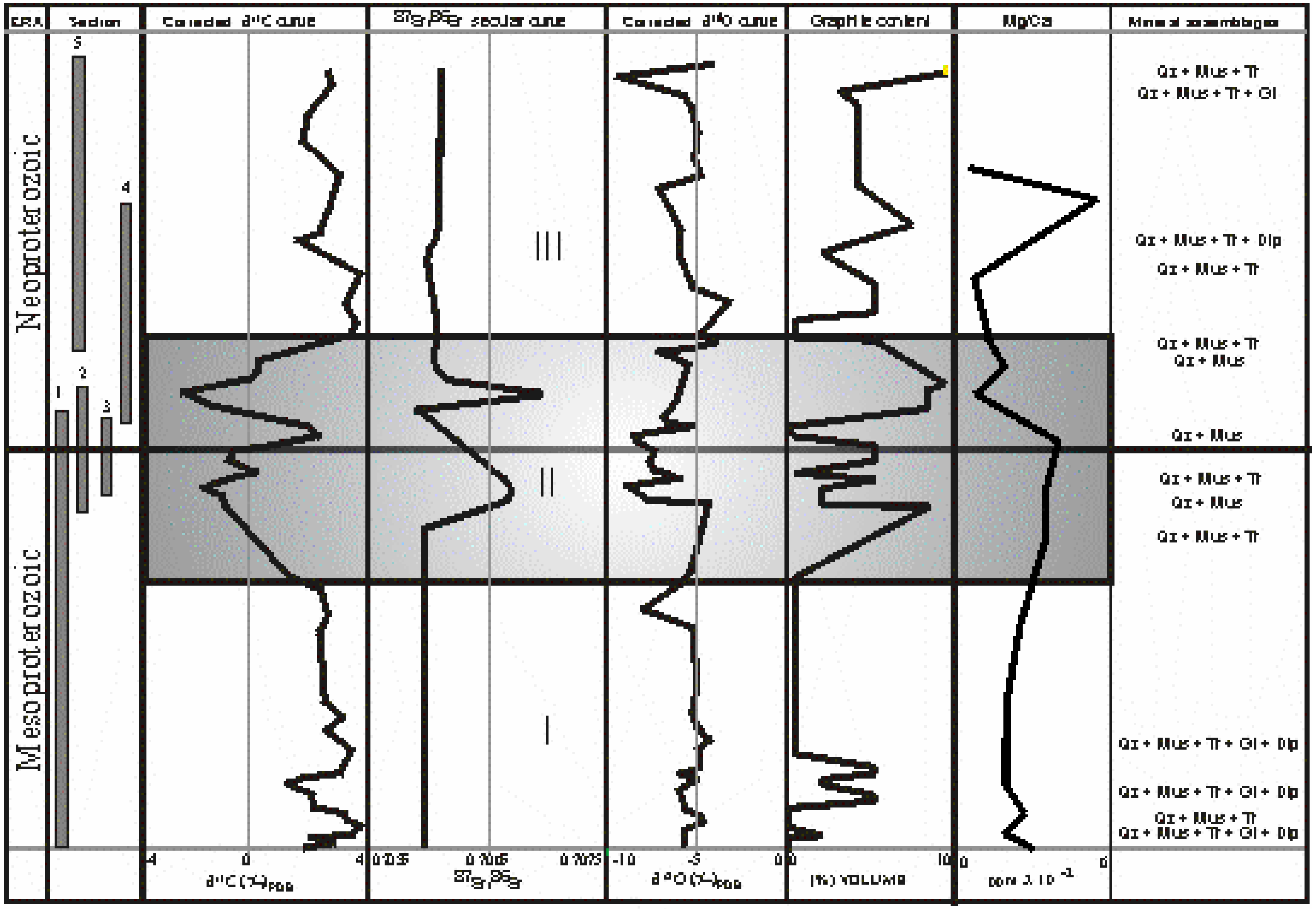
ERA
Section
Corrected δ13C curve
87Sr/86Sr secular curve
Corrected δ18O curve
Graphite content
Mg/Ca
Mineral assemblages
Neoproterozoic
Mesoproterozoic
1
2
3
4
5
III
II
I
-4
0
4
δ13C (‰)PDB
0.7035
0.7055
0.7075
87Sr/86Sr
-10
-5
0.0
δ18O (‰)PDB
0
10
(%) VOLUME
0
6
ppm x 10 -1
Qz + Mus + Tr
Qz + Mus + Tr + Gl
Qz + Mus + Tr + Dlp
Qz + Mus + Tr
Qz + Mus + Tr
Qz + Mus
Qz + Mus
Qz + Mus + Tr
Qz + Mus
Qz + Mus + Tr
Qz + Mus + Tr + Gl + Dlp
Qz + Mus + Tr + Gl + Dlp
Qz + Mus + Tr
Qz + Mus + Tr + Gl + Dlp

FIGURE 6

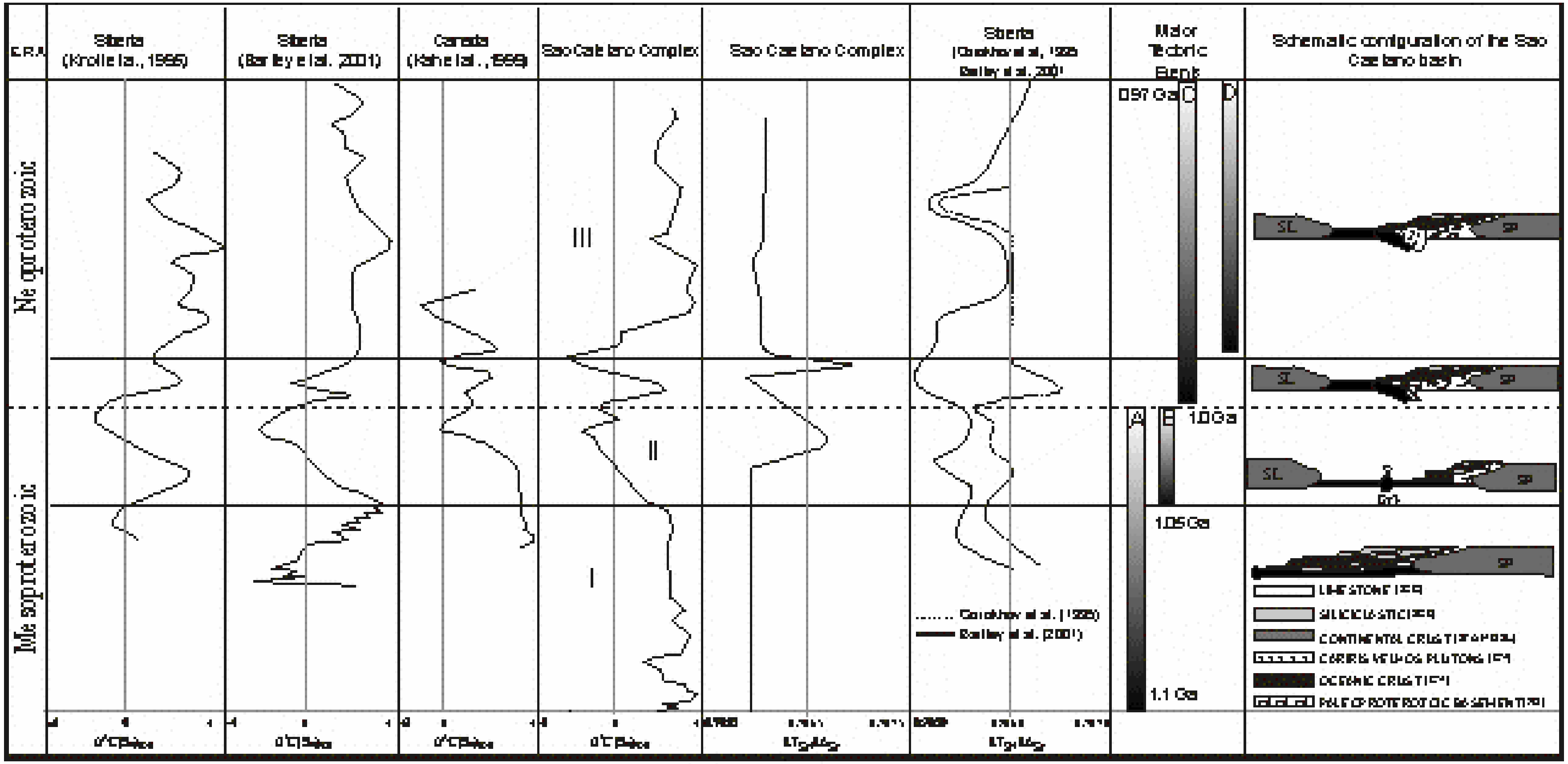
ERA
Siberia (Knoll et al., 1995)
Siberia (Bartley et al. 2001)
Canada (Kah et al., 1999)
Sao Caetano Complex
Sao Caetano Complex
Siberia (Gorokhov et al., 1995; Bartley et al. 2001)
Major Tectonic Events
Schematic configuration of the Sao Caetano basin
Neoproterozoic
Mesoproterozoic
III
II
I
0.97 Ga
C
D
A
B
1.0 Ga
1.05 Ga
1.1 Ga
SL
SP
Gorokhov et al. (1995)
Bartley et al. (2001)
LIMESTONE
SILICICLASTIC
CONTINENTAL CRUST
CARRIS VELHOS PLUTONS
OCEANIC CRUST
PALEOPROTEROZOIC BASEMENT
δ¹³C‰
⁸⁷Sr/⁸⁶Sr
0.7050

FIGURE 7

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Yours sincerely,
For the Editor,

Kathleen Hair
CHEMGE Editorial Office
Amsterdam

PRESERVATION OF THE SEDIMENTARY C-ISOTOPE SIGNATURE IN MARBLES: AN ASSESSMENT OF THE USE OF HIGH RESOLUTION C-ISOTOPE STRATIGRAPHY

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Keywords: C, O and Sr isotopes, chemostratigraphy, graphite-calcite thermometry, Meso-Neoproterozoic marbles, Brazil.

Running title: Preservation of Sedimentary C- Isotope Signature in Marbles

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ABSTRACT

Amphibolite-facies marbles of the São Caetano Complex (SCC), Borborema structural province, northeastern Brazil, show near primary (sedimentary) $\delta^{13}C_{c\ (calcite)}$ values (from -2.2 to +3.7‰$_{PDB}$), which fall into the range for $\delta^{13}C_c$ values of Meso-Neoproterozoic limestone successions. However, some anomalous negative C-isotope shifts (up to 4‰ $_{PDB}$) are interpreted as the result of modifications of the C-isotope composition during metamorphism, caused by diffusion of CH_4 (derived from ^{12}C-rich organic matter) into calcite. Absence of anomalous ^{13}C-rich carbonate samples indicate that C-isotope fractionation associated to diffusion of ^{13}C-rich CO_2 (from graphite or from silicate-carbonate reactions) into calcite did not occur. This contention is supported by uncoupled behavior of $\delta^{13}C_c$ and $\delta^{18}O$ values. Geochemical indicators falling into accepted ranges for unaltered Meso-Neoproterozoic limestone (e.g. average Sr contents of 1500 ppm, Mn/Sr ratios from 0.006 to 0.140, and Rb/Sr ratios between 0 and 0.005) indicate that the element and isotope compositions of the precursor limestone were buffered prior to the activity of metamorphic fluids. This suggests that the undepleted $\delta^{13}C_c$ and $^{87}Sr/^{86}Sr$ (from 0.706 to 0.707) values for the SCC marbles reflect the isotope signature of the Meso-Neoproterozoic seawater from which the limestone protoliths were deposited.

Co-variation of $\delta^{13}C_c$ and $\delta^{13}C_{g\ (graphite)}$ values suggests that calcite-organic matter fractionation during metamorphism was homogeneous in all of the studied marbles. Slight enrichments in the $\delta^{13}C_g$ values and further depletions in the $\delta^{13}C_c$ ones may have resulted from stronger organic matter-calcite C-isotope fractionation during metamorphism as a consequence of high organic matter/graphite contents (8%). Metamorphism temperatures, between 514 and 761°C, estimated from calcite-graphite C-isotope thermometry are in agreement with the temperature range deduced from the paragenesis calcite-quartz-muscovite-tremolite-diopside-garnet. Anomalously high metamorphic temperatures (up to 1075°C) were also estimated from samples with the highest graphite contents and, hence, the more depleted $\delta^{13}C_c$ values, nevertheless, these metamorphic temperatures are considered artifacts. Since there is no petrographic evidence of retrograde metamorphism, it is proposed that anomalous $\delta^{13}C_c$ depletions observed in the SCC marbles occurred during prograde regional metamorphism.

1. Introduction

Variations in the C, O and Sr-isotope composition of marine carbonates have been successfully used to determine changes in the isotope geochemistry of ancient oceans (Veizer and Hoefs, 1976). The chemostratigraphic technique has been extensively used with great success in well-preserved Phanerozoic limestone successions (Scholle et al., 1986; Mitchell et al., 1996), and even in Proterozoic ones, in which strong post-depositional alterations of the isotope signatures are common (Kaufman et al., 1991; Derry et al., 1992).

The reliability of the chemostratigraphic approach, however, depends on whether the original isotope composition of limestones was preserved after their deposition (Kaufman et al., 1991). Diagenesis and/or metamorphism have been considered as the main processes that affect the original isotope composition of carbonates because of increase of temperature or interaction with diagenetic/metamorphic fluids (Banner and Hanson, 1990; Kaufman et al., 1991). Modifications of the isotope composition of carbonates have been also related to: (1) presence of organic matter, graphite and/or silicates; (2) interaction with primary or secondary internal and external fluids holding different isotope composition; (3) presence of different carbonate phases; and (4) extent of fluid-rock interaction during precipitation, deposition and post-depositional processes (Brand and Veizer, 1980a, b; Veizer, 1983; Banner and Hanson, 1990; Kaufman et al., 1991).

Several approaches have been adopted to investigate post-depositional alteration of isotope signatures in carbonate sequences, and to avoid misleading chemostratigraphic results (Kaufman et al., 1991; Derry et al., 1992). Nevertheless, these approaches have been largely applied to sedimentary successions and their efficiency on metamorphosed examples has remained an open question (Melezhik et al., 2001; Melezhik and Fallick, 2003).

This study aims to evaluate possible causes of anomalously depleted $\delta^{13}C_c$ values observed in the C-isotope chemostratigraphic profiles of graphite-bearing and graphite-rich marbles, from the São Caetano Complex (SCC), northeastern Brazil, which although show $\delta^{13}C_c$ values between -2.2 and + 3.7 ‰$_{PDB,}$ falling within the ranges for late Meso-early Neoproterozoic limestone, show some anomalous negative $\delta^{13}C_c$ shifts (as large as 4‰) jeopardizing the chemostratigraphic interpretations (Silva et al., submmited). It also aims assessing the reliability of the application of C-isotope stratigraphy to marbles and establishing the conditions under which such anomalous C-isotope depletions took place. Finally, the accuracy of the elemental and isotopic indicators used to assure the reliability of chemostratigraphic studies is assessed by applying a multivariable approach, in which the methods used by Kaufman et al. (1991) and Melezhik et al. (2001) (e.g elemental and isotope geochemistry of marbles, petrography, cathodoluminescence) are complemented by analyses of the graphite C-isotope composition, classifications of the mineralogical assemblages and use of C-isotope thermometry (calcite-graphite).

2. Geological setting and age

The SCC is a metavolcano-sedimentary sequence composed of garnet-biotite paragneiss, quartzite, marble, metadacite, metarhyolite, and metabasalt, which occur in the Alto Pajeú Terrane, Transversal Domain of the Borborema structural province, northeastern Brazil (Fig. 1). The studied marbles are interbedded with metagraywacke successions and present variable thickness, which diminishes up-section. They are mainly calcitic and contain silicate mineral assemblages typical of amphibolite facies (quartz- muscovite-tremolite- diopside- garnet; Silva et al., submitted, Fig. 2). These marbles also contain considerable amounts of graphite, which are found either disseminated or disposed in layers, whose abundance and thickness increase up-section (Fig. 3).

FIGURE 1

The age of the SCC is poorly constrained. The oldest age (>1.3 Ga, U-Pb) proposed to this complex was inferred from Archean to Late Mesoproterozoic detrital zircons collected from metagraywackes in its uppermost portion (Brito Neves et al., 2002).The youngest age has been assumed from a 0.96 Ga U-Pb age for a granodioritic-biotite orthogneiss that intruded the metagraywacke successions overlying the studied marbles (Kozuch, 2003). According to Silva et al. (submitted), the original limestone sequences (marble precursors) of the São Caetano Complex were deposited between 1.1 and 0.97 Ga. The SCC was strongly affected by widespread shearing and folding, however, no direct dating of the metamorphism has been done and the regional metamorphism has been attributed to the Brasiliano event (0.75-0.5 Ga; Brito Neves et al., 2002; Gomes, 1999).

3. Analytical techniques

Marble samples were examined in thin-section to determine their mineral paragenesis. Cathodoluminiscence (CL) analyses were also performed to support the petrographic analyses. The CL examination of rock slabs was done by using a Nuclide Corporation ELM-3R Luminoscope attachment mounted on an Olympus zoom stereomicroscope at the University of São Paulo. Test observations were made using both low power (7.5kV/0.5mA) and high power (15 kV/1 mA) electron beams, and defocused to cover elliptical areas of about 2.5-3cm x 1.5-2.0cm, corresponding to beam powers of ~1.3 and ~3.3 μa.mm^{-2}, respectively. The vacuum was held at about 50 mtorr.

Determinations of minor and major elements were performed using X-Ray fluorescence in a Rigaku RIX 3000 XRF unit equipped with a Rh tube, at the XRF Laboratory, Department of Geology, Federal University of Pernambuco. Analyses of major and minor elements are reported in parts per million (ppm) (Table 1).

For carbonate C- and O-isotope analyses, micro-drilled carbonate samples were reacted with 100% orthophosphoric acid during 12 hours at 25^{o}C (3 days when dolomite was apparently present). The CO_2 released from this reaction was extracted in a high-vacuum extraction line by using cryogenic cleaning according to the method proposed by Craig (1957). The CO_2 samples were analyzed for C and O- isotopes in a double-inlet gas source, triple-collector mass spectrometer (Sira II), at the Stable Isotope Laboratory (LABISE), Department of Geology, Federal University of Pernambuco. The isotopic compositions were contrasted against the in-house standard Borborema Skarn Calcite (BSC), which calibrated against the NBS-18, NBS-19 and NBS-20 standards, shows an isotopic composition of $\delta^{18}O = -1.28 \pm 0.04‰_{PDB}$ and $\delta^{13}C = -8.58 \pm 0.02‰_{PDB}$.

For determination of the Sr-isotopic composition, 5 mg of powdered carbonate sample were leached in 0.5 M ultraclean acetic acid, and centrifuged to obtain purified Sr. Rb and Sr were separated from the leachates by standard ion-exchange techniques. 500 to 1000 ng of purified Sr together with 1μg H_3PO_4 were loaded onto a Ta filament for TIMS analysis on a seven collector Mat 262 instrument at the Geochronology Laboratory, Institute of Geosciences, University of Brasilia.

For graphite C-isotope analyses, 5 mg of pure and clean graphite were hand picked after dissolving all the carbonate fraction of the marbles by treating 5g of grounded sample with 30% acetic acid for four hours. About 0.25 mg of pure graphite were analyzed for C-isotopes in a Finnigan Delta Plus Advantage instrument at the Department of Geology of the State University of Rio de Janeiro (UERJ). The reproducibility of the analyses is better than ~0.05 ‰. Graphite C-isotope data are reported relative to the PDB scale.

4. Results and Discussion

4.1 Petrography and cathodoluminescence

Modifications in the element and isotope composition of carbonates are usually accompanied by changes in their mineralogical, textural and luminescence features (Fairchild and Spiro, 1987; Fairchild et al., 1990; Derry et al., 1992). Reduction in the carbonate crystal size and the presence of bright yellow, orange-red to red CL, which is activated by Mn concentrations as low as ~1 ppm and is just perceptible at Mn concentrations above 10 ppm, when usually violet colors are visible, have been regarded as the most diagnostic features forecasting such modifications (Marshall, 1988, 1992; Kaufman et al., 1991; Kaufman and Knoll, 1995; Habermann et al., 1998; Kah et al., 1999).

Based on these assumptions, petrographic and cathodoluminescence (CL) characterizations of selected samples were performed to predict elemental and isotopic modifications and to discriminate against potentially altered samples.

Petrographic analyses show that the studied marbles are well-crystallized and mainly calcitic. A fining-up tendency is observed in the calcite crystal size, which is very variable (between 0.8 and 4 mm; Fig.2 A1, B1) within and between the stratigraphic sections (Fig. 3). Calcite does not present exsolution textures, except when in contact with graphite, whose modal content reaches up to 8%. Graphite presents a coarsening-up tendency (up to 5 mm), and are randomly distributed (disseminated and/or in layers) within the stratigraphic sections (Fig. 3). Silicate phases are also found in these marbles (quartz, muscovite, tremolite, diopside, garnet) but in negligible amount (<0.5% on average; Fig. 2 A_1,B_1).

FIGURE 2

CL analyses, on the other hand, reveal overgrowths on calcite grains, which are better seen in reflected light as thin white films (Fig. $2A_2$, B_2). The typical Mn-activated, bright orange to red CL, is usually absent; whereas dull CL predominates (Fig. $2A_3$). Dull red or violet CL was found only in one sample from the Sitio dos Nunes section (Fig $2B_3$) and light blue CL was observed in isolated grains of one sample from the Pedra de Cal section (Flor 5).

Our first screen for isotopically modified samples shows that no signs of modifications in the elemental and isotopic compositions are present in the studied marbles. Thus all samples were considered for the chemostratigraphic characterization of the carbonates successions, regardless the metamorphism to which they were submitted. However, some samples with predominant dull CL, high graphite contents and reduced calcite crystal-size (Table 1) show anomalously depleted $\delta^{13}C_c$ values (see discussion below). This suggests that the application of CL analyses in the prediction of modifications in the C-isotope composition of carbonates seems to not always properly work. Limitations of CL in the selection of isotopically unmodified samples have already been noted by other authors, although it does represent a useful filter to be complemented by other observations (e.g. Kaufman et al., 1991; Kaufman and Knoll, 1995; Kah et al., 1999).

Since high graphite contents and reduced calcite crystal-sizes are common and diagnostic features of samples affected by graphite-calcite C-isotope fractionation during metamorphism (Dunn and Valley, 1992; Kitchen and Valley, 1995; Satish-Kumar et al., 2002), it is suggested that the anomalous depletions in the $\delta^{13}C_c$ values can be related to the presence of graphite. The mineral parageneses, typical of amphibolite facies, coupled with the lack of retrogression signs, indicate that the original limestone sequences were only subjected to a prograde regional metamorphic event.

Finally, high Fe concentrations are proposed here as the cause of suppressions of the Mn activated (bright) CL, since XRF analyses show that most of the analyzed samples contain Mn concentrations above 10 ppm and Fe contents up to 1400 ppm (see the following section and Table 1).

4.2 Elemental and isotopic geochemistry

$\delta^{13}Cc$ values between -2.2 and + 3.7 $‰_{PDB}$ and $^{87}Sr/^{86}Sr$ ratios between 0.706 and 0.707 were observed in the SCC marbles. These values fall within the expected ranges of Meso-Neoproterozoic limestone and are believed to reflect those of the seawater from which the original limestones were precipitated (Silva et al., submitted; Fig. 3). However the occurrence of some samples with anomalously depleted $\delta^{13}C_c$ values (excursions up to 4$‰_{PDB}$), which are not observed in the well preserved sedimentary counterparts (Kah et al., 1999; Bartley et al., 2001), indicates that modifications of their original C-isotope composition could have occurred after deposition of their sedimentary protoliths.

The geochemical values, on the other hand, fall within the ranges proposed by Brand and Veizer (1980a) for unaltered marine limestones (Sr contents between ~800 and ~2100 ppm, with an average of 1500 ppm, Rb < 10 ppm, Mn 10-85 ppm, Fe 500-2000 ppm; Table 1, Fig. 3). The geochemical ratios (Mn/Sr < 1, Rb/Sr < 0.2, Ca/Sr < 0.004; Table 1) fall into the ranges for Meso-Neoproterozoic limestone sequences worldwide whose isotope compositions reflect that of their precursor seawaters (Kah et al., 1999, 2001; Bartley et al., 2001). Since no anomalous elemental concentrations and/or ratios were observed, it is also proposed that the element geochemistry of the marble may well reflect that of their sedimentary precursors.

The geochemical values reported above indicate that although the elemental composition of the studied marbles preserved the original composition of their sedimentary precursor, in some cases, the isotopic signature seem to have not been preserved. Since slight modifications of the carbonates isotope composition can be accompanied by pronounced changes in their values of global geochemistry (Brand and Veizer, 1980a, b; Veizer, 1983) when submitted either to diagenesis or metamorphism, the reliability of the reported isotope and elemental data need to be further evaluated in order to assure the validity of the chemostratigraphic record.

4.3 Geochemical screen for isotopically modified samples

Changes in Sr/Mn, Ca/Sr and Sr/Rb ratios, accompanying modifications of the isotope signature of carbonates, are often recognized and attributed to post-depositional processes (Brand and Veizer, 1980a, b). Mn/Sr = 3, Rb/Sr = 0.5 and Ca/Sr = 0.1 have been proposed as the upper limits to identify possible modifications of the original isotope composition of marine carbonates, and used to screen for possible modifications in the isotope composition and to investigate their possible causes (Brand and Veizer, 1980a, b; Veizer, 1983; Kaufman et al., 1991; Derry et al., 1992; Bartley et al., 2001; Melezhik et al., 2001).

Since the elemental composition of the SCC marbles fall within the above mentioned ranges, establishing whether the anomalously depleted $\delta^{13}C_c$ values represent primary (sedimentary) signatures, or whether they are a consequence of modifications of the C-isotope composition after deposition, has remained relatively difficult. In order to overcome with this problem, a combination of the isotopic and elemental approaches proposed by Kaufman et al. (1991), Kaufman and Knoll (1995), Melezhik et al. (2001) and Melezhik and Fallick (2003) (Fig 4a-f, 5a-d), and detailed petrographic studies and determinations of the C-isotope composition of graphite was used (Fig. 6a-d, 7 a-d).

The application of the correlation diagrams proposed by Kaufman et al. (1991) shows that although most of the studied marbles seem to have preserved the original C- and O-isotope composition of their parent sediments, modifications in the C- and O-isotope composition of some samples seem to have occurred since coupled depletions in their $\delta^{13}C_c$ and $\delta^{18}O$ values are present (Fig. 4a). Nevertheless, the modified nature of these samples can be considered as artifacts since they do also fall into the fields of unaltered limestones when contrasting their isotope composition against some elemental indicators (see alteration trends in Figs. 4b-4f).

FIGURE 4

The correlation diagrams proposed by Melezhik et al. (2001) and Melezhick and Fallick (2003) also show that most samples fall within the fields of isotopically unmodified limestone (Fig.5 a). This suggests that the C and Sr-isotope compositions of the SCC marbles represent that of the seawater from which their sedimentary precursors were deposited. Although some samples presenting high $^{87}Sr/^{86}Sr$ ratios and low $\delta^{13}C_c$ values seem to have undergone modifications in their Sr-isotope composition, the uncoupled variation of the $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ values (Fig. 5b) and the slight variability of the $\delta^{18}O$ ones (Fig 4a, 5b) further account for the unmodified nature of their Sr-isotope signature. Even though this is at odds with the alteration trends observed when contrasting the $^{87}Sr/^{86}Sr$ ratios against the most sensitive elemental indicators (e.g. Mn/Sr, Mg/Ca, Fig 5 c,d), Mn/Sr ratios < 1 and Mg/Ca ratios < 0.02 preclude with this idea.

FIGURE 5

The complementary analyses proposed here (Fig 6a,d, 7a) show a negative correlation between the C and O-isotope composition of carbonates and the graphite contents; the samples with the highest graphite contents usually having the lowest $\delta^{13}C_c$ and $\delta^{18}O$ values (Fig. 6a). Major $\delta^{13}C_c$ depletions were found in samples in which graphite is agglutinated and disposed in layers (Fig 6b) and also in samples with larger graphite flakes (Fig. 6c). Conversely, depletions in the $\delta^{13}C_c$ values occur independently of the presence and proportions of the silicate minerals (Fig. 6d). Major depletions in the $\delta^{13}C_c$ values were found in samples with the lowest graphite C-isotope compositions ($\delta^{13}C_g$ values, Fig. 7b).

FIGURE 6

On the basis of the results reported above, it can be envisaged that the unusual depleted $\delta^{13}C_c$ values observed in some the studied carbonates are related to the former presence of ^{12}C-depleted organic matter. These anomalous depletions would have resulted from organic matter-calcite C-isotope fractionation during prograde metamorphism, independently of modifications in the elemental and O and Sr-isotope compositions. This suggests that the coupled behavior of the C and O-isotope chemostratigraphic curves in the studied carbonates does not necessarily point out post-depositional modification of the isotope signature, and thus represent original secular variations of the isotope composition of the sedimentary precursors.

Finally, since the O and Sr-isotope composition of carbonates is significantly more affected than the C-isotope one, by the action of invading fluids during diagenesis and/or metamorphism, modifications of the C-isotope composition of the studied marbles by these means can be discarded. This idea is further supported by the element geochemistry which resembles that of coeval limestone successions and suggests that the sedimentary protoliths were effectively buffered by ocean water during early diagenesis.

4.4 Evaluation of possible mechanisms of modification of the C-isotope composition in the São Caetano Complex marbles

Several authors (e.g. Bottinga, 1969; Shieh and Taylor, 1969; Arita and Wada, 1990; Chacko et al., 1991; Kaufman et al., 1991; Dunn and Valley, 1992; Melezhik et al., 2001; Melezhik and Fallick, 2003) have investigated the possible causes of modifications in the isotope composition of organic mater/silicate-rich carbonates during metamorphism. For instance, depletions in the carbonate $\delta^{13}C_c$ and $\delta^{18}O$ values during contact and regional metamorphism have been identified and attributed to silicate-carbonate reactions involving the generation of ^{13}C-rich and ^{18}O-rich CO_2 fluids (Shieh and Taylor, 1969; Winkler, 1979). Progressive depletions in the carbonate C-isotope values and concomitant increases of the graphite C-isotope ones have also been identified in graphite-bearing marbles, and attributed to diffusion of ^{12}C-rich CH_4 (released from organic matter) into calcite (Dunn and Valley, 1992; Kitchen and Valley, 1995).

Increases in the carbonate $\delta^{13}C$ values, on the other hand, have been attributed to diffusion of ^{13}C-rich CO_2 derived organic matter/graphite into calcite, but its occurrence depends on whether it takes place in a closed (buffered) system or not (Evans et al., 2002 and references therein). Modifications in the O-isotope composition of carbonates has been attributed to this process, but have not been identified during diffusion of graphite released CH_4 into carbonate (Chacko et al., 1991; Bergfeld et al., 1996; Evans et al., 2002). Modifications in the $^{87}Sr/^{86}Sr$ values related to incorporations of external fluids can also occur, but they depend on the fluid/rock ratios (Derry et al., 1992; Bickle et al., 1997).

Considering that the SCC marbles contain both silicate minerals and graphite, any of the above-mentioned mechanisms may have been responsible for the anomalous depleted $\delta^{13}C_c$ values. Nevertheless, since the depletions are not related to the presence of silicate minerals (Fig. 6d), but to the presence of graphite, an evaluation of the mechanisms involving organic matter/graphite in modifications of the C-isotope composition of carbonates is necessary.

In order to determine these mechanisms, further determinations of the C-isotope composition of coexisting graphite ($\delta^{13}C_g$) and carbonates ($\delta^{13}C_c$) were performed in samples whose sedimentary C-isotope composition seems to have been potentially preserved (undepleted) and in samples in which potential modifications (anomalously depleted $\delta^{13}C_c$ values) seem to have occurred. Samples were selected from two stratigraphic sections based on the coherence of the C-isotope chemostratigraphic pathways (see selected samples in Table 1).

Comparisons between $\delta^{13}C_c$ and $\delta^{18}O$ values reveal that the isotope composition of some of the samples presenting anomalous depleted $\delta^{13}C_c$ values can be considered as unmodified, since almost constant $\delta^{18}O$ values predominates (Fig. 7a). On the other hand, positive correlations between the $\delta^{13}C_c$ and $\delta^{13}C_g$ values of both potentially modified and unmodified samples were observed (Fig. 7b). Nevertheless, uncoupled variations of the $\delta^{13}C_c$ and $\delta^{13}C_g$ values of potentially modified and unmodified samples within single sections were also observed. Lower calcite-graphite C-isotope fractionation values ($\Delta\ ^{13}C_c$-C_g) were also observed in potentially modified samples within single sections. A negative correlation was observed when contrasting the $\Delta\ ^{13}C_c$-C_g and $\delta^{13}C_g$ values. No correlation was observed between the $\Delta\ ^{13}C_c$-C_g and $\delta^{13}C_c$ values (Figs. 7c-d).

FIGURE 7

Three lines of evidence point to closed-system diffusion of organic matter/graphite- derived CH_4 into calcite as the most likely process that should have modified the C-isotope composition of the SCC marbles during metamorphism:

1) The highest $\delta^{13}C_c$ values (~3‰ $_{PDB}$) observed in some of the potentially unmodified samples fall into the expected ranges for Meso-Neoproterozoic sequences (Fig. 8). If diffusion of organic matter/graphite derived CO_2 into calcite had occurred, higher $\delta^{13}C_c$ values and modified $\delta^{18}O$ ones would have also occurred, since the CO_2 resulting from this process is ^{13}C-rich; and external O-rich fluids are needed to account for its formation during volatilization of organic matter. Since the SCC marbles seem to have remained as a closed system, as shown by the element geochemistry, incorporation of external O-rich fluids is unlikely and thus formation of ^{13}C-rich CO_2 derived from graphite discarded.

2) Smaller $\Delta\ ^{13}C_c$-C_g values were identified in isotopically modified samples with the higher $\delta^{13}C_g$ values (Fig 7c). Since during diffusion of organic matter/graphite-derived ^{12}C-rich CH_4 into calcite, graphite becomes more depleted in ^{12}C and calcite becomes enriched in that isotope, lowering the $\Delta\ ^{13}C_c$-C_g values, this process is proposed as the responsible of the anomalously depleted $\delta^{13}C_c$ values.

3) Slight changes in the $\delta^{13}C_c$ values with respect to the $\Delta\ ^{13}C_c$-C_g ones were observed between potentially modified and unmodified samples; however the lower the $\delta^{13}C_c$ values of isotopically modified samples, the lower the $\Delta\ ^{13}C_c$-C_g values (Fig. 7d). This kind of behavior discards the possibility of diffusion of ^{13}C-rich CO_2 (derived from organic matter/graphite) into calcite as the mechanism leading to depleted $\delta^{13}C_c$ values, since during such a process the $\delta^{13}C_g$ and $\delta^{13}C_c$ values are expected to decrease and increase respectively concomitantly with increases in the $\Delta\ ^{13}C_c$-C_g values. This in turn may indicate that the calcite-graphite C-isotope fractionation occurred heterogeneously within single sections.

4.5 Calcite-graphite thermometry

Considering that a C-isotope fractionation between calcite and organic matter/graphite was invoked to explain anomalous depletions in the $\delta^{13}C_c$ values of some the studied marbles; and that this process is temperature dependent (Bottinga, 1969; Valley and O'Neil , 1981; Wada and Suzuki, 1983; Dun and Valley, 1992; Kitchen and Valley, 1995; Valley, 2001; Evans et al. 2002), isotopically modified (depleted $\delta^{13}C_c$ values) and unmodified (no depleted $\delta^{13}C_c$ values) samples from two different stratigraphic sections were used to estimate the temperature at which such a C-isotope fractionation occurred. These samples were also selected to evaluate the effect of modifications in the C-isotope composition of carbonates on the metamorphic temperature estimates (MT), since the proposed calcite-graphite isotope fractionation occurred heterogeneously within single sections. MT estimates were performed by using the equation by Dunn and Valley (1992), given that the co-variation of our calcite-graphite fractionation values and temperature estimates are quite similar to those reported elsewhere, which used this equation (Table1, Figs 8 a-b). Nevertheless, MT were also estimated from the equation Kitchen and Valley (1995) to assure the reliability of the data.

After applying the equation of Dunn and Valley (1992) MP between 578° and 1075°C and between 514° and 761°C were estimated for the Pedra de Cal and Rodiador sections respectively (Fig. 8c). Higher MT estimates were obtained from the equation of Kitchen and Valley (1995) for samples falling above the 650°C isograd of Dunn and Valley (1992) (Fig. 8b-d). The opposite behavior is observed below such an isograd. MT as low as 452°C and as high as 2191°C were also estimated from the equation of Kitchen and Valley (1995), but considered as artifacts since they are not in agreement with the mineral paragenesis (calcite, quartz, muscovite, tremolite, diopside, garnet).

Based on the above results, it is suggested that calcite-graphite C-isotope fractionation affecting some of the SCC marbles occurred at temperatures between 514 and 761°C. This is supported by the MT estimated from the equation of Dunn and Valley (1992) which are in good agreement with me mineral paragenesis. The application of the equation of Kitchen and Valley (1995) seems to have yielded on incongruent MT. Although our results show that the studied marbles where subjected to a very wide range of temperatures, it is proposed that differences in MT estimates within/between stratigraphic sections are due to the following factors: (1) Secular variations the $\delta^{13}C_g$ values (higher MT are observed in samples with similar $\delta^{13}C_c$ values and more enriched $\delta^{13}C_g$ ones within/between sections (Fig. 8d). Co-variation of the $\delta^{13}C_g$ values and the MT estimates supports this contention and also explains the higher MT estimated for the Pedra de Cal section, which present lower $\delta^{13}C_c$ values (Figs. 8 c-d, 9, Table 1). (2) Altered nature of the $\delta^{13}C_c$ values and variable graphite contents. Samples whose $\delta^{13}C_c$ values had been potentially lowered always yielded on temperatures above the 650^{o}C, whereas isotopically unmodified samples yielded temperatures below this value (Fig. 8b). Although the highest MT (>800^{o}C) was estimated for one isotopically unmodified sample, it seems to have resulted from its higher graphite contents (>8%), and hence the further alteration of its graphite C-isotope composition (Figs 8 c-d, 9, Table 1). (3) Variations in graphite disposition within the stratigraphic section. This factor seems to have favored the C-isotope exchange between graphite and calcite and thus the MT estimates, since major depletions in the $\delta^{13}C_c$ values and smaller fractionation values were found in samples in which graphite is agglutinated and disposed in layers (Figs 6c,b, 9).

Finally, since no retrograde textures were observed in the marbles and the graphite was not armored by other minerals, it is proposed that the ^{12}C-rich CH_4 – calcite diffusion process causing modified (depleted) $\delta^{13}C_c$ values occurred during prograde-regional metamorphism.

FIGURE 8

FIGURE 9

5. CONCLUSIONS

The C, O and Sr- isotope composition of the Meso-Neoproterozoic São Caetano Complex marbles seem to reflect the original isotope composition of the seawater the original limestone (marble protoliths) were deposited from. Nevertheless, some anomalous depletions in the $\delta^{13}C_c$ values (up to 4‰), hampering the chemostratigraphic analyses were considered as artifacts, and resulted from diffusion of ^{12}C-rich CH_4 (derived from organic matter/graphite) into calcite during metamorphism (see corrected and uncorrected $\delta^{13}C_c$ secular variation curve in Fig. 9). These modifications were favored by high graphite contents and by the layered accumulation of graphite within the marbles. Alterations in the C-isotope composition associated to silicate-calcite reactions, which generally involve generation of ^{13}C-rich CO_2, are absent.

Modifications of the C-isotope composition of carbonates resulting from incorporation of external fluids, holding different isotopic composition, during both, diagenesis and metamorphism, is unlikely, since excellent buffering the original limestone sequences (marble precursors) seems to have occurred prior to metamorphism. This is evidenced by the unaltered nature of samples demonstrated in geochemical screen (Sr contents average 1500 ppm, Mn/Sr ratios from 0.006 to

0.140, and Rb/Sr ratios between 0 and 0.005), which resembles that of well preserved Meso-Neoproterozoic limestone, and by the slightly variable O (from -6 to -10‰) and Sr (from 0.706-0707) isotope signature of samples that underwent C-isotope change. This also indicates that the SCC marbles preserved the isotope composition of their sedimentary precursor even after metamorphism. This suggests that modifications of the C- isotope composition of organic matter-bearing and organic matter-rich carbonates can occur during metamorphism independently of modifications in their Sr-isotope and elemental composition.

The observed depletions in the $\delta^{13}C_c$ values seem to have occurred at temperatures varying from 514 to 761°C, as estimated from the calcite-graphite thermometry. These temperatures, coupled with absence of retrograde signs in the marbles, suggest that the ^{12}C-rich CH_4-calcite diffusion, leading to the anomalous depleted $\delta^{13}C_c$ values, occurred under prograde metamorphism (amphibolite-facies). The estimated metamorphic temperature range is in good agreement with the mineral paragenisis (calcite, quartz, muscovite, tremolite, diopside, garnet). Although temperatures as high as 1075°C were estimated, they seem to be related to larger changes in the calcite and graphite C-isotope compositions, resulting from the presence of high amounts of graphite (up to 8%). Differences in the metamorphic temperature estimates from unaltered samples belonging to a single stratigraphic section were also observed and resulted from variations in the graphite C-isotope composition. This factor has been ignored by many other authors and need to be taken into account when using the calcite-graphite thermometer.

Finally, our results indicate that since modifications in the C-isotope composition of graphite-bearing and graphite-rich marbles can take place independently of variations in the O and Sr-isotope and elemental geochemistry, the sole application of the traditional geochemical approaches (e.g. Kaufman et al., 1991, Kaufman and Knoll, 1995, Melezhik et al., 2001 and Melezhik and Fallick, 2003) should be considered with caution when working with these kind of lithologies, given the complexity of processes involved during diagenesis and metamorphism. For chemostratigraphic purposes, a union of the methods proposed by Kaufman et al. (1991), Melezhik et al. (2001) and Melezhik and Fallick (2003) with those herein proposed seems to be the most appropriated approach on the identification of post-depositional modifications in the C-isotope composition of graphite-rich marbles. It is important mentioning that our results preclude with the idea that coupled depletions in the $\delta^{13}C_c$ and $\delta^{18}O$ values of marine carbonates reflect modifications in the carbonates isotope signature, and that modifications in their isotope composition are accompanied by modifications in the elemental geochemistry. They instead suggest that if coherent secular variation pathways of both, $\delta^{13}C_c$ and $\delta^{18}O$ values, are found, the preservation of the primary (sedimentary) isotope signatures of marbles can be assured.

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Sample	Heigh (m)	$\delta^{13}C_c$ (‰$_{PDB}$)	$\delta^{18}O$ (‰$_{PDB}$)	$\delta^{13}C_{gr}$ (‰$_{PDB}$)	Δ^{13}Cc-Cg	MT (K-V)	MT D-V)	Graphite (%)	Graphite Size (cm)	Mineral assembla.	$^{87}Sr/^{86}Sr$	Mn (ppm)	Mg (ppm)	Sr (ppm)	Rb (ppm)	Ca (ppm)	Fe (ppm)
Flor 1	0	1.9	-6.5					0				57	3910	1401	10	362200	1792
Flor 2	0.8	2.7	-6.4					0									
Flor 3	1.6	2.0	-6.5					0									
Flor 4	2.1	3.3	-6.3	-2.08	5.4	538	578	2				12	2000	1274	2	328000	760
Flor 5	3.5	3.7	-5.4					0		QMTGD	0.706	10	1980	1578	0	407970	249
Flor 6	4.4	3.2	-5.6					0									
Flor 7	5.5	3.1	-6.2					0									
Flor 8	6.5	2.0	-6.5					0									
Flor 9	7	1.9	-6.2					5									
Flor 10	8.5	2.0	-6.5					5		QMT		78	3450	1259	0	384250	1670
Flor 11	10.3	1.2	-5.7					2									
Flor 12	11.1	1.7	-6.4					2		QMTGD							
Flor 13	12.1	3.0	-5.6					5									
Flor 14	13.1	3.1	-5.6	-1.23	4.3	638	644	5				6	0	1586	1	405000	1065
Flor 15	15.2	3.3	-5.6					0.5		QMTGD		11	2040	1572	0	405780	309
Flor 16	16.5	3.2	-5.2					0.5									
Flor 17	18.8	2.5	-5.7					0.5									
Flor 18	20.9	3.0	-5.9					0.5									
Flor 19	23.5	2.4	-5.8					0.5									
Flor 20	24.5	2.5	-5.7					0.5									
Flor 21	34.5	2.3	-5.9					0.5	0.1	QMTDG		10	2070	1738	0	404050	515
Flor 22	37.5	2.6	-8.1					0.5	0.1-0.3	QMGTD							
Flor 23	41.5	2.3	-6.5					0.5									
+Flor 24	43.5	1.3	-5.9	-1.07	2.3	959	810	8	0.2-0.3								
*Flor 25	53.5	0.2	-4.7					8				24	3870	2487	0	483780	991
+Flor 26	54.7	-0.8	-5.1					8									
Flor 27	55.7	-0.4	-5.6					8									
*+Flor 28	57	-1.6	-5.8	-3.53	1.9	1102	864	8	0.2-0.3								
*Flor 29	58.5	-2.2	-5.9					8									
*+Flor 30	60.	-1.5	-6.2					8									
*+Flor 31	62	-1.5	-6.5	-2.08	0.6	2192	1075	8	0.2-0.3								
*Flor 32	65	-1.8	-12.8					5									

+Flor 33	68	0.2	-7.7	-4.24	-4.04	625	637	5	0.1-0.3								
*+Flor 34	70	-1.4	-13.6	-5.46	4.1	658	657	5	0.1-0.3			51	3700	2583	7	350400	9038
*Flor 35	74	-1.3	-11.4					5				85	4830	2101	1	360400	2976
Flor 36	76	-0.7	-8.8					5									
*Flor 37	79	-2.0	-11.6					5	0.2-0.4	QM		95	6500	1053	4	287500	2837
*+Flor 38	82	-1.4	-7.5	-5.03	3.7	714	690	5	0.2-0.3	QM		30	3600	2488	3	302500	3980
Flor 39	86	1.7	-6.0					0			0.706	9	3500	1643	0	317700	913
Flor 40	96	0.1	-8.9					0									
Flor 41	98	-0.8	-8.1					0	0.2	QM							
Flor 42	102	-0.8	-8.5					1									
*Flor 43	105	-0.9	-10.3					1									
Flor 44	110	-0.8	-7.0					1									
Malu 1	0	-0.7	-8.3					2		QMT							
Malu 2	2.3	-0.9	-9.3					2									
Malu 3	3.5	-1.5	-7.0					2									
Malu 4	5	-0.7	-8.3					5									
Malu 5	6	0.2	-8.5					0.5									
Malu 6	8	-0.7	-8.3					5				10	10370	822	0	394590	230
Malu 7	9.5	-0.5	-9.1					5									
Malu 8	10.5	0.9	-9.2					5									
*Malu 9	11	-0.5	-11.1					0.5	<0.1	QMT							
Malu10	12	2.3	-6.6					0.5									
Malu11	12.5	2.3	-7.7					0.5									
Malu12	13.5	2.0	-7.9					0									
Malu13	15.5	-0.8	-6.8					5									
Malu14	16	-0.8	-7.1					5									
Malu15	16.5	-0.3	-6.9					5				29	2900	2142	0	400610	382
Malu16	19.5	0.2	-7.5					5									
Malu17	20.5	0.2	-7.6					5	0.2-0.3	QM							
Malu18	21.5	-0.6	-7.5					5	0.3-0.5	QM							
Malu19	24.5	-0.9	-8.1					5									
*Malu20	25	-1.7	-14.0					5									
*Malu21	26	-1.7	-14.0					5				65	4000	2014	10	366180	5164
*Malu22	27	-1.1	-13.9					5									

Malu23	28	-0.9	-9.7					5									
Nunes 1	0	-2.6	-7.5					5	0.6-0.4	Q M		79	6350	1658	22	349890	2201
Nunes 2	1.2	-2.2	-6.0					5			0.707	47	5200	690	5	313700	1733
Nunes 3	2.2	-2.4	-6.6					5									
Nunes 4	4.2	-1.5	-9.7					5									
Nunes 5	5.7	-2.1	-6.8					8	0.5-0.8	QMTG							
Nunes 6	9.2	-2.3	-6.1					8				51	10490	552	10	379950	1757
Nunes 7	11.2	2.4	-7.6					0.5									
Nunes 8	12.7	-1.1	-6.6					8	0.3	QMT	0.706	38	3930	1968	0	363310	5520
*Nunes 9	14.7	-2.2	-8.6					8			0.706	81	6330	574	10	382460	1939
Nunes 10	15.7	-0.9	-9.0					8									
Rod 1	0	-1.5	-8.4					5	0.6	QMT	0,707	21	5990	765	10	345500	1617
+Rod 2	10	3.4	-11.2	-3.34	6.8	452	514	5	0.3								
Rod 3	12	3.7	-10.1					5				80	4130	1107	10	371210	1234
+Rod 4	15	3.3	-7.1	-1.66	5.0	575	603	5	0.3			53	3600	1187	10	293500	1221
Rod 5	20	3.8	-7.7					2									
*Rod 6	21.5	-1.8	-14.0					5	0.3	QMT	0.706	36	4300	1801	10	302000	4372
*+Rod 7	22.5	-1.6	-10.8	-4.43	2.8	850	761	5	0.3								
Rod 8	24.5	2.0	-7.7					5									
Rod 9	27	-0.1	-8.6					5				9	22580	970	0	377500	493
*+Rod 10	29	-0.9	-10.6	-4.02	3.1	799	736	5	0.3			73	3900	2599	10	300600	2728
Rod 11	31	0.2	-8.6					4									
+Rod 12	33	1.5	-6.7	-4.65	6.2	485	540	4	0.3			45	3440	1464	10	375130	1463
Rod 13	36	2.1	-7.0					4									
Rod 14	40	1.7	-6.9					4									
+Rod 15	44	1.9	-7.1	-3.48	5.4	543	581	4	0.2-0.3			21	1200	1603	10	385000	1369
Rod 16	46	2.2	-7.5					3	0.2-0.3	QMTG	0.706	11	3700	1944	10	304900	1208
+Rod 17	49	2.7	-10.5	-3.05	5.8	513	560	8	0.3								
Rod 18	51	2.6	-6.2					8	0.3	QMT							
Rod 19	56	0.4	-6.8					8									
Rod 20	60	-0.5	-7.5					8									
*Santros 1	0	-1.9	-7.3					8									
*Santros 2	0.5	-1.7	-7.4					8									
Santros 3	6	0.0	-7.4					8									

Santros 4	7	0.3	-6.8					8			0.706	18	3000	2145	10	319600	1439
Santros 5	9	0.3	-8.2					0.5	0.5-1.0	QM		13	6530	1966	10	393780	1200
Santros 6	9.5	0.3	-7.1					0.5									
Santros 7	10.5	1.0	-6.1					0.5									
*Santros 8	12	0.3	-6.7					0.5	0.3	QMT		15	5050	2178	0	390090	1129
*Santros 9	17	-0.6	-5.5					0.5			0.706	24	2300	2041	10	322600	913
*Santros 10	18	0.5	-6.0					0.5									
Santros 11	19	1.8	-8.2					0.5									
Santros 12	20	2.2	-7.8					0.5		QMT							
Santros 13	20.5	2.4	-7.4					0.5				10	2010	1557	0	402850	384
Santros 14	21.5	2.3	-7.5					0.5									
Santros 15	23.5	2.4	-7.6					5									
Santros 16	25.5	1.8	-6.8					5									
Santros 17	27.5	1.5	-7.3					5									
Santros 18	29.3	2.4	-7.5					0.5	0.3	QMTD		10	3290	2006	0	396990	734
Santros 19	30.5	2.5	-7.3					0.5									
Santros 20	33.5	2.7	-7.1					0.5			0.706	10	2100	2077	10	331400	828
Santros 21	38.5	3.1	-8.4					0.5		QMTD							

Table 1. Geochemical data for the studied marble samples from the Sao Caetano Complex. Asterisks indicate potentially altered samples. Crosses indicate samples selected for metamorphic temperatures (MT). MT were calculated by using the equations of (D-V) Dunn and Valley (1992) and (K-V) Kitchen and Valley (1995). ($\Delta^{13}C_c$-C_g) calcite-graphite fractionation values.

FIGURE CAPTIONS

Figure 1. Geologic map of the studied area. Numbers represent the location of the stratigraphic sections: 1.Pedra de Cal, 2. Santa Rosa, 3. Malutagem, 4. Rodiador. Tectonic terranes map adapted from Ferreira et al. (1998). Geologic map modified from Gomes (1999).

Figure 2. Main petrographic and luminescence characteristics observed in the SCC marbles. A) Flores 2, Pedra de Cal section), B) Nunes 2, Sitio dos Nunes section. Coarse-sized calcite crystals are commonly identified in thin section (A_1, B_1) and in sample slabs by using reflected light (A_2,B_2). CL photomicrographs show the low to non-luminescent nature of the SCC marbles (A_3-B_3).

Figure 3. Lithologic, isotopic and elemental stratigraphy of the studied marbles. (A) Pedra de Cal, (B) Malutagem, (C) Sito dos Nunes, (D) Rodiador, (E) Santa Rosa. All sections show an opposite behavior between the carbonate C-isotope ($\delta^{13}C_c$) and O-isotope ($\delta^{18}O$) secular variation curves. Note the mimetic behavior of the graphite ($\delta^{13}C_g$) and carbonate ($\delta^{13}C_c$) C-isotope secular curves in the Pedra de Cal and Rodiador sections. Also note the opposite behavior between the $\delta^{13}C_c$ and the graphite content secular curves in all sections.

Figure 4. Cross-plots of isotopic and elemental data obtained from the SCC marbles. Arrows indicate geochemical post-depositional alteration trends as proposed by Derry et al. (1992) and Kaufman et al. (1991). Note that most samples fall into the unaltered fields, suggesting that marbles probably preserved the C and O-isotope composition of the original limestone sequences. In A, numbers indicate the average fields for the isotope composition for the different marble

successions: 1) Rodiador, 2) Pedra de Cal, 3) Sitio dos Nunes, 4) Santa Rosa, 5) Malutagem.

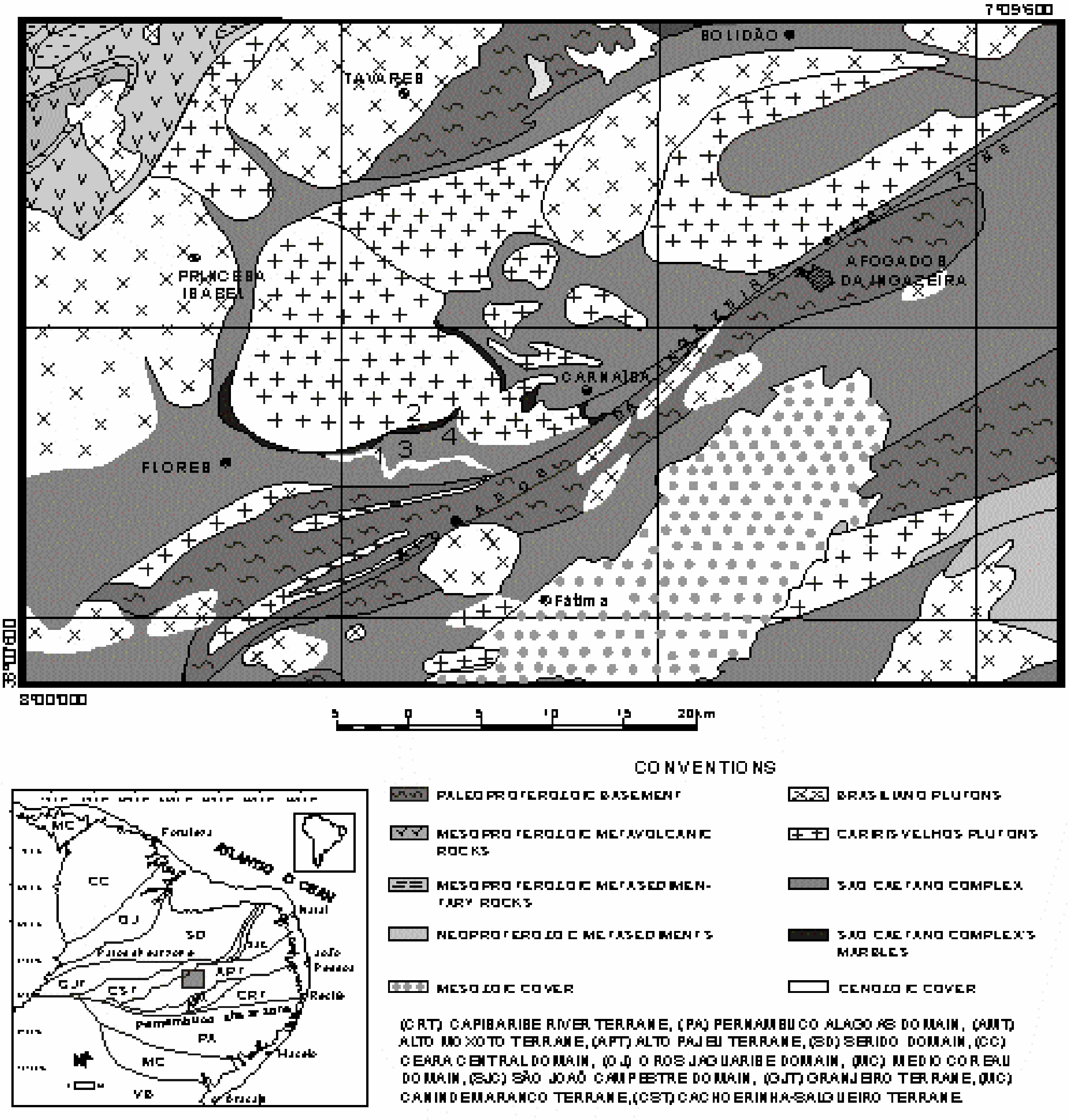
Figure 5. Cross-plots of the isotope and elemental data from the SCC marbles. Arrows indicate geochemical post-depositional alteration trends as proposed by Melezihk et al., 2001 and Melezihk and Fallick, 2003. Non alteration trends were identified, indicating that must likely the Sr-isotope composition of the original limestone successions was preserved.

Figure 6. Cross-plots showing variations in the C and O -isotope signature of selected samples (see Table 1) with respect to graphite contend (A), graphite disposition (B), graphite crystal size (C) and silicate assemblages (D). Arrows indicate geochemical post-depositional alteration trends as proposed by Derry et al. (1992) and Kaufman et al. (1991).

Figure 7. Cross-plots of the isotope data obtained for selected carbonate and graphite samples of the SCC. A) Variations in the calcite C ($\delta^{13}C_c$) and O ($\delta^{18}O$) isotope composition. Arrows show the alteration trends as proposed by Derry et al. (1992) and Kaufman et al. (1991). B) Variation in the $\delta^{13}C_c$ and graphite C-isotope values ($\delta^{13}C_g$). Arrows show the good positive correlation between the $\delta^{13}C_c$ and $\delta^{13}C_g$ values in both unaltered and altered samples. C) Variation between the calcite-graphite fractionation values ($\Delta^{13}C_c$-C_g) and the $\delta^{13}C_g$ values. Arrow shows the negative correlation between $\Delta^{13}C_c$-C_g and $\delta^{13}C_g$ in both unaltered and altered samples. Also note that altered samples show smaller $\Delta^{13}C_c$-C_g values than the unaltered ones. D) Variations between the $\Delta^{13}C_c$-C_g and the $\delta^{13}C_c$ values. Observe the negative correlation between $\Delta^{13}C_c$-C_g and $\delta^{13}C_c$ (see arrow) and the more depleted $\delta^{13}C_c$ shown by altered samples.

Figure 8. Variations of the metamorphic temperature (MT) estimates with respect to: calcite graphite fractionation values ($\Delta^{13}C_c$-C_g) (A, B) and the calcite ($\delta^{13}C_c$) and graphite ($\delta^{13}C_g$) C-isotope composition (C,D). In A and B lines represent the MT tendencies calculated by: (D-V) Dunn and Valley (1992), (K-V) Kitchen and Valley (1995), (P-K) Polyakov and Kharlashina (1995) and those from this work. Lines in C and D represent the MT estimated by Kitchen and Valley (1995) and Dunn and Valley (1992) respectively. Other conventions refer to Fig. 7.

Figure 9. Composite litho and chemostratigraphic columns of the SCC marble successions. Conventions in the lithostratigraphic column are the same that in Figure 3. Arabic numbers indicate the stratigraphic position of the studies marbles successions: 1. Pedra de Cal, 2. Malutagem, 3. Sitio dos Nunes, 4. Rodiador, 5. Santa Rosa. Stratigraphic variations in the mineral assemblages are also shown: quartz (Qz), muscovite (Mus), tremolite (Tr), diopside (Dip), garnet (Gt). The unaltered and altered $\delta^{13}Cc$ secular curves were constructed after screening for post-depositional signs. Note the mimetic behavior of the carbonate ($\delta^{13}C_c$) and graphite ($\delta^{13}C_g$) C-isotope secular variation curves. Also note the inverse behavior of the $\delta^{13}C_c$ and $\delta^{13}C_g$ curves with respect to the graphite contend one. Note the mimetic behavior between variations in the $\delta^{13}C_g$ and metamorphic temperatures (MT). Roman numbers indicate the C-isotope stages characterized by Silva et al. (submitted).



(CRT) CAPIBARIBE RIVER TERRANE, (PA) PERNAMBUCO ALAGOAS DOMAIN, (AMT) ALTO MOXOTO TERRANE, (APT) ALTO PAJEU TERRANE, (SD) SERIDO DOMAIN, (CC) CEARA CENTRAL DOMAIN, (OJ) OROS JAGUARIBE DOMAIN, (MC) MEDIO COREAU DOMAIN, (SJC) SÃO JOAÕ CAMPESTRE DOMAIN, (GJT) GRANJEIRO TERRANE, (MC) CANINDE MARANCO TERRANE, (CST) CACHOERINHA-SALGUEIRO TERRANE

FIGURE 1

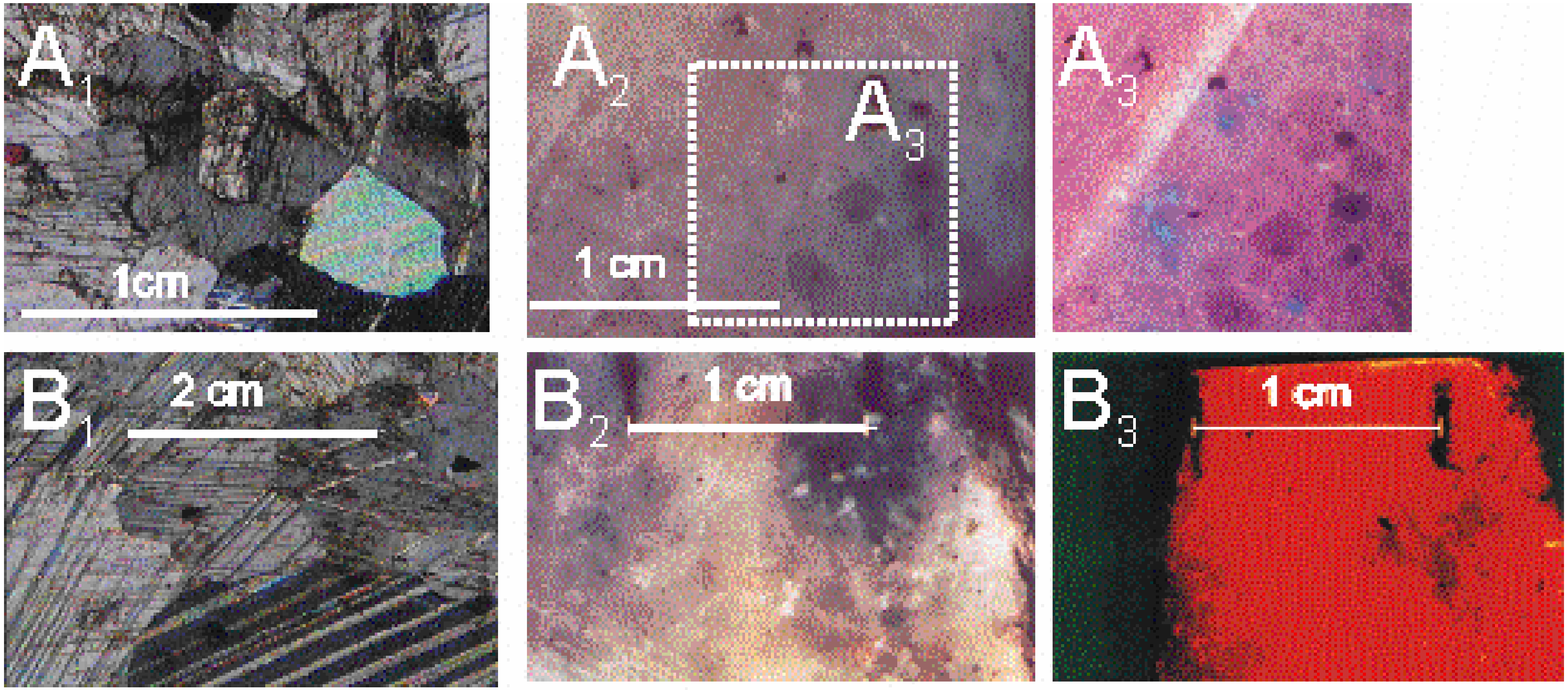


FIGURE 2

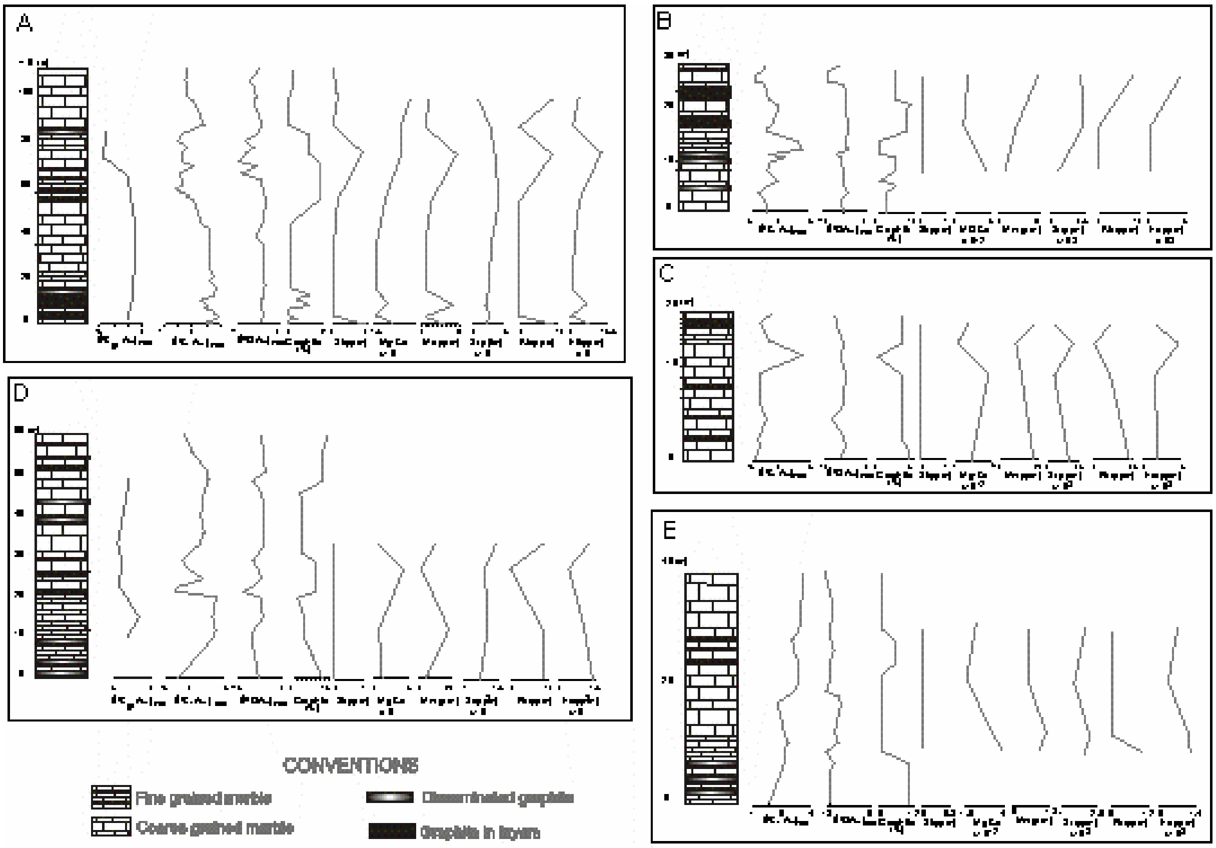

A
B
C
D
E
CONVENTIONS
Fine grained marble
Coarse grained marble
Disseminated graphite
Graphite in layers

FIGURE 3

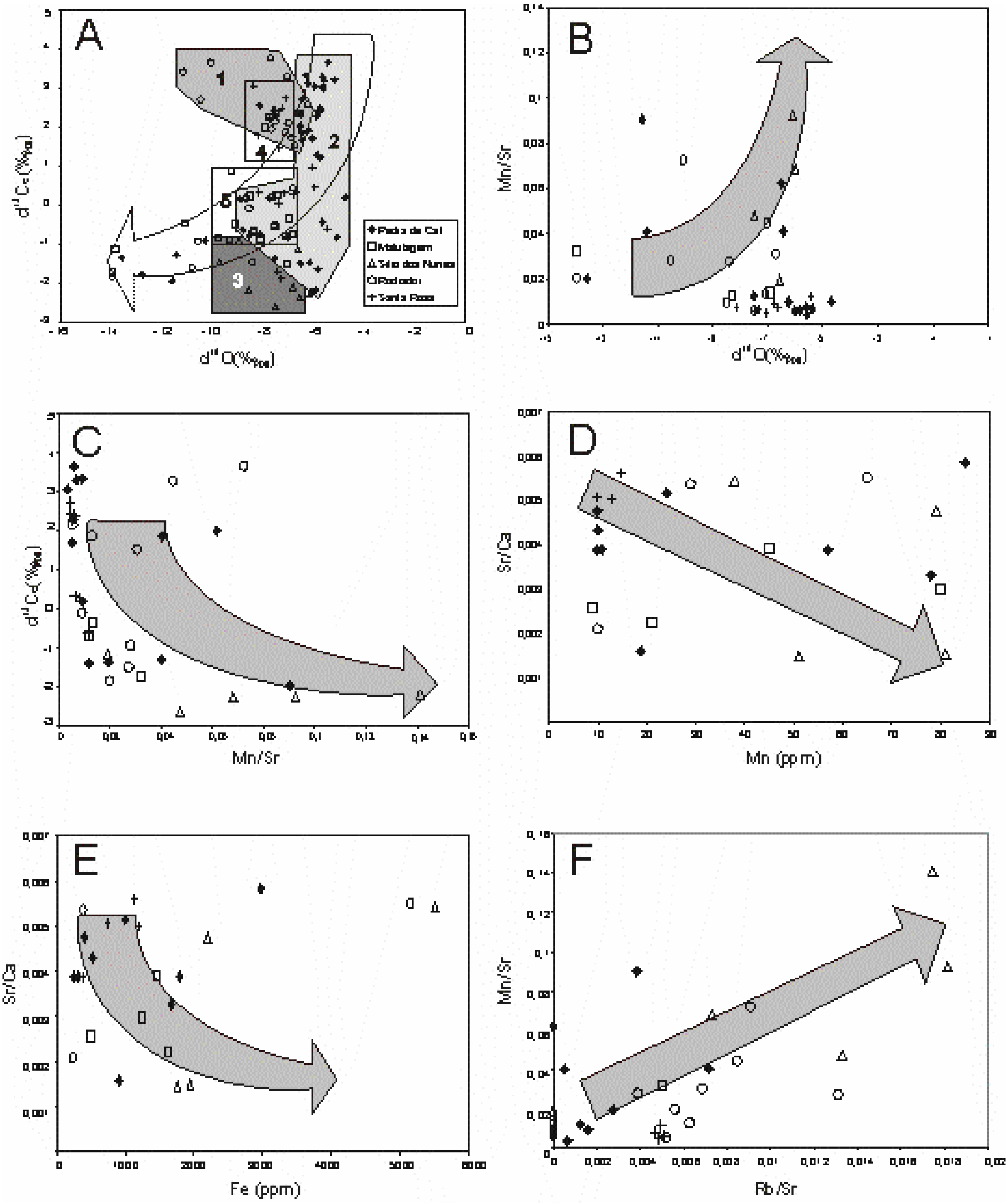

A
d¹³Cc(‰PDB)
d¹⁸O(‰PDB)
1
2
3
4
5
Pedra de Cal
Malulagem
Sítio dos Nunes
Rodador
Santa Rosa
B
Mn/Sr
d¹⁸O(‰PDB)
C
d¹³Cc(‰PDB)
Mn/Sr
D
Sr/Ca
Mn (ppm)
E
Sr/Ca
Fe (ppm)
F
Mn/Sr
Rb/Sr

FIGURE 4

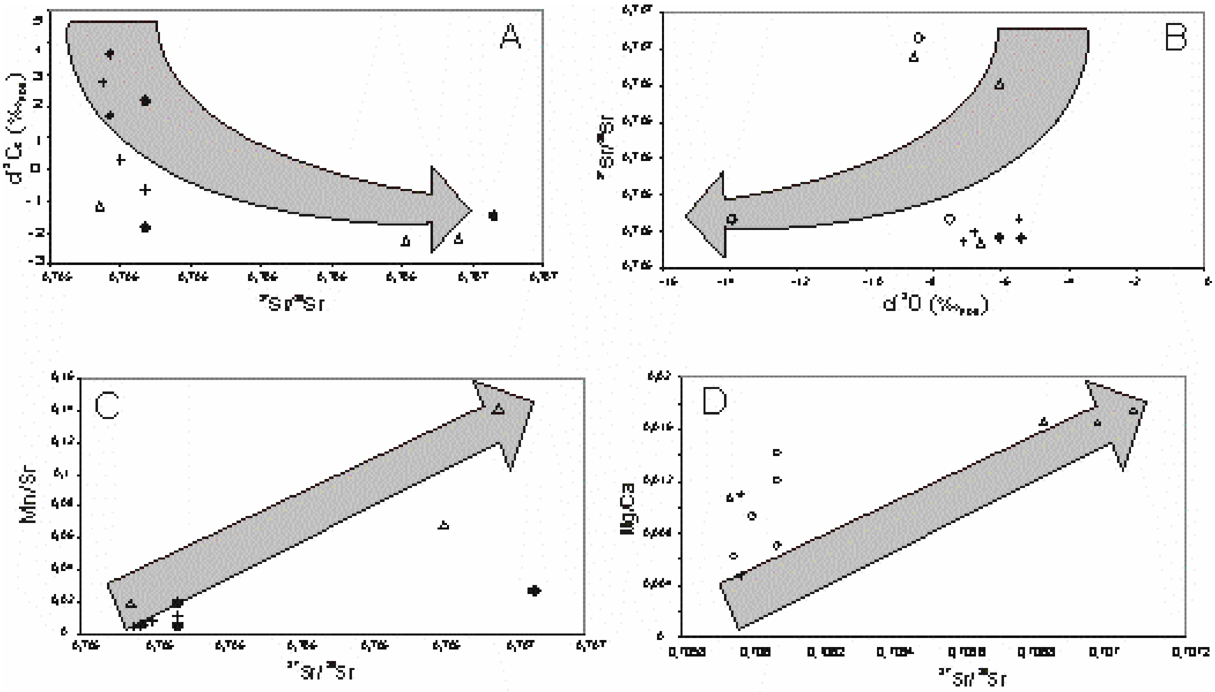

A
d13Cc (‰PDB)
5
4
3
2
1
0
-1
-2
-3
87Sr/86Sr
B
87Sr/86Sr
d18O (‰PDB)
-16
-14
-12
-10
-8
-6
-4
-2
0
C
Mn/Sr
0,16
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
87Sr/86Sr
D
Mg/Ca
0,2
0,16
0,12
0,08
0,04
0
0,7058
0,706
0,7062
0,7064
0,7066
0,7068
0,707
0,7072
87Sr/86Sr

FIGURE 5

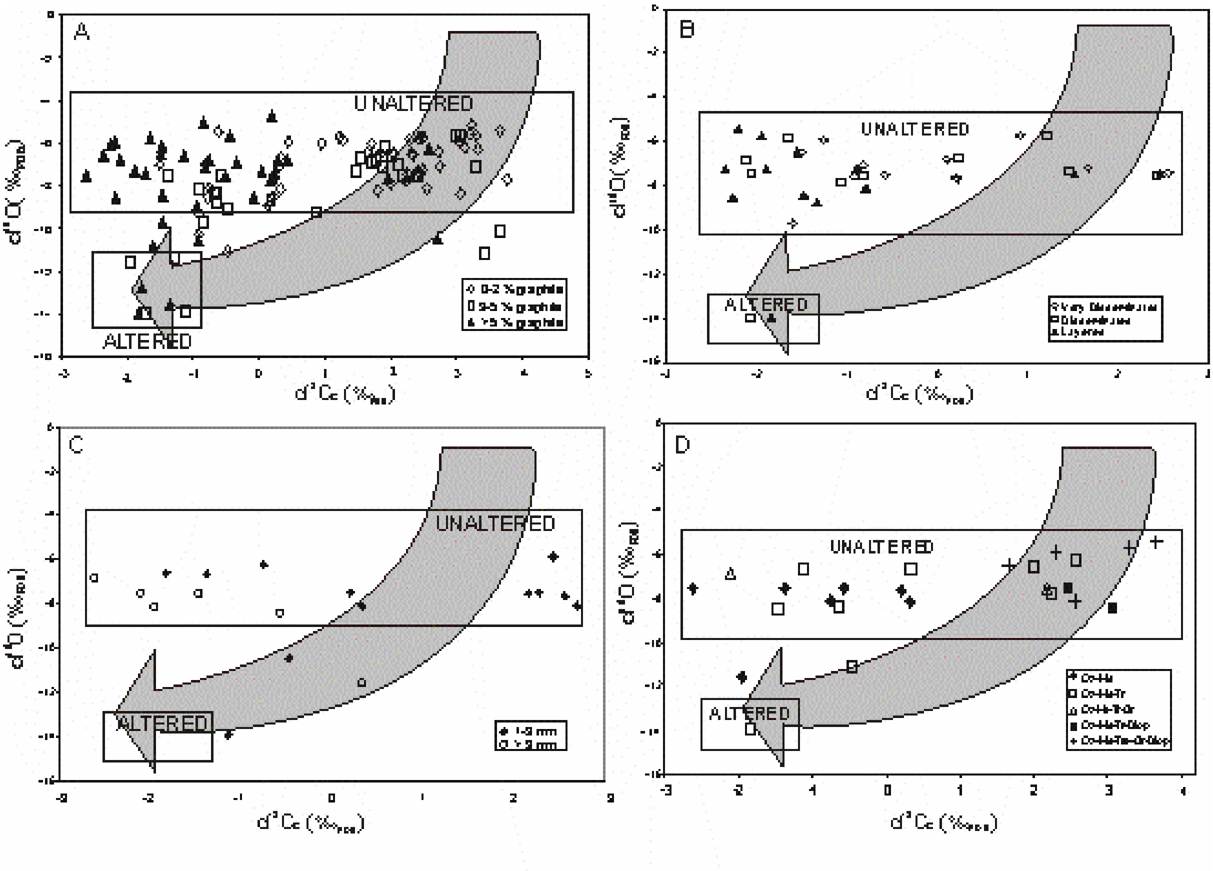

A
UNALTERED
ALTERED
0-2 % graphite
3-5 % graphite
> 5 % graphite
d¹⁸O (‰VPDB)
d¹³Cc (‰VPDB)
B
UNALTERED
ALTERED
Very Disseminated
Disseminated
Layered
d¹⁸O (‰VPDB)
d¹³Cc (‰VPDB)
C
UNALTERED
ALTERED
1-3 mm
> 3 mm
d¹⁸O (‰VPDB)
d¹³Cc (‰VPDB)
D
UNALTERED
ALTERED
Cc-Hu
Cc-Hu-Tr
Cc-Hu-Tr-Or
Cc-Hu-Tr-Diop
Cc-Hu-Trm-Or-Diop
d¹⁸O (‰VPDB)
d¹³Cc (‰VPDB)
-3
-2
-1
0
1
2
3
4

FIGURE 6

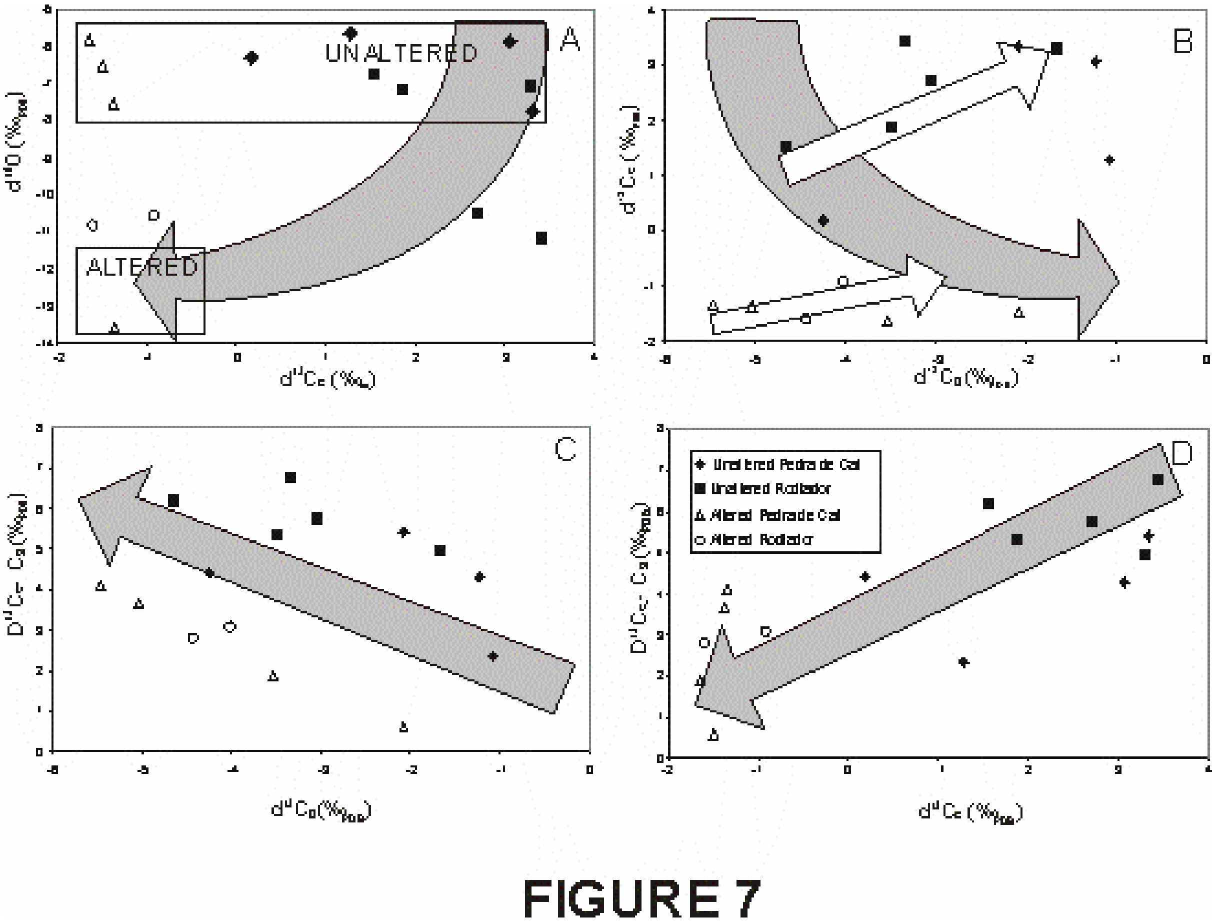

A
UNALTERED
ALTERED
d18O (‰PDB)
d13Cc (‰PDB)
B
d13Cc (‰PDB)
d13Co (‰PDB)
C
D13Cc- Co (‰PDB)
d13Co(‰PDB)
D
Unaltered Pedra de Cal
Unaltered Rodiador
Altered Pedra de Cal
Altered Rodiador
D13Cc- Co (‰PDB)
d13Cc (‰PDB)

FIGURE 7

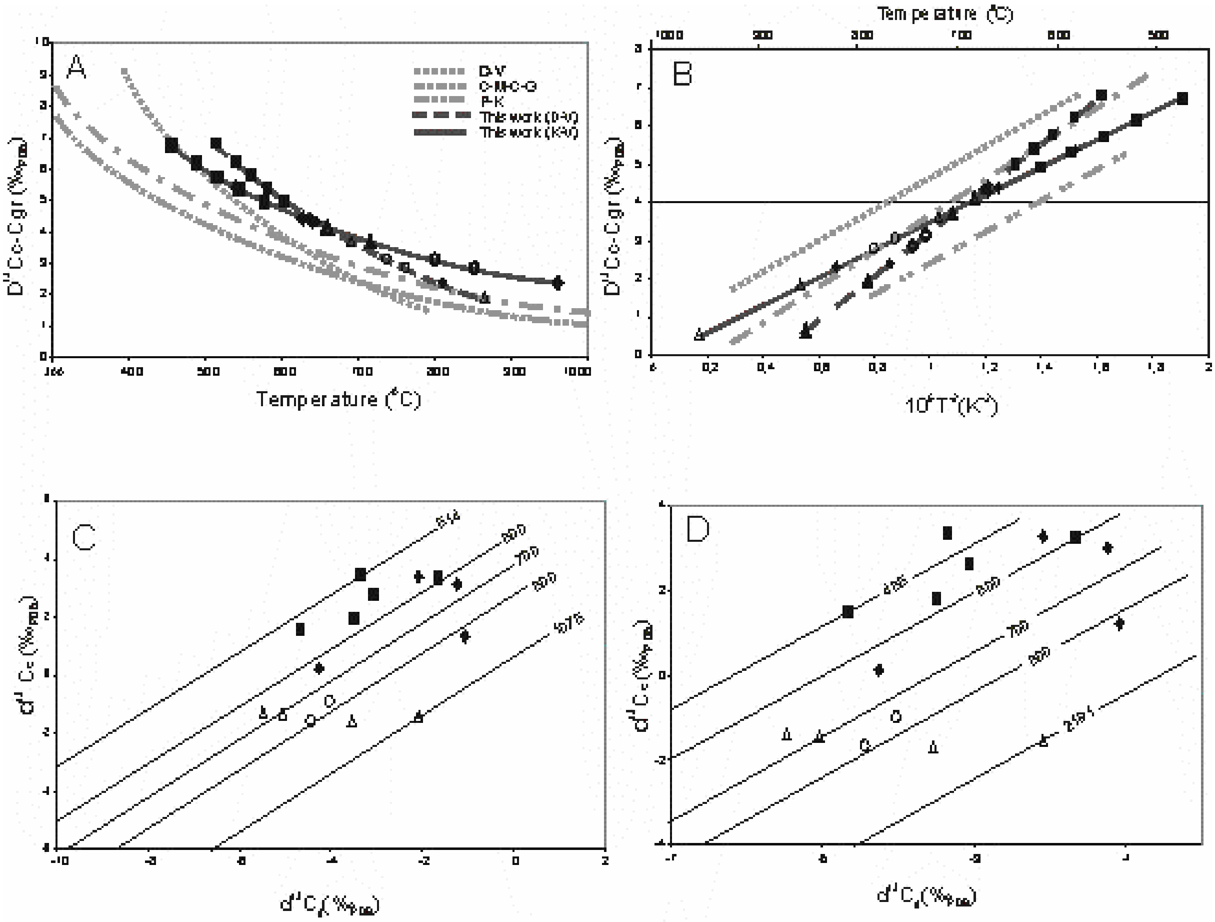

A
D-V
C-M-C-G
P-K
This work (D-V)
This work (K-V)
Temperature (°C)
B
Temperature (°C)
1000
900
800
700
600
500
10⁶T⁻²(K⁻²)
C
514
600
700
800
1075
D
486
600
700
800
2191

FIGURE 8

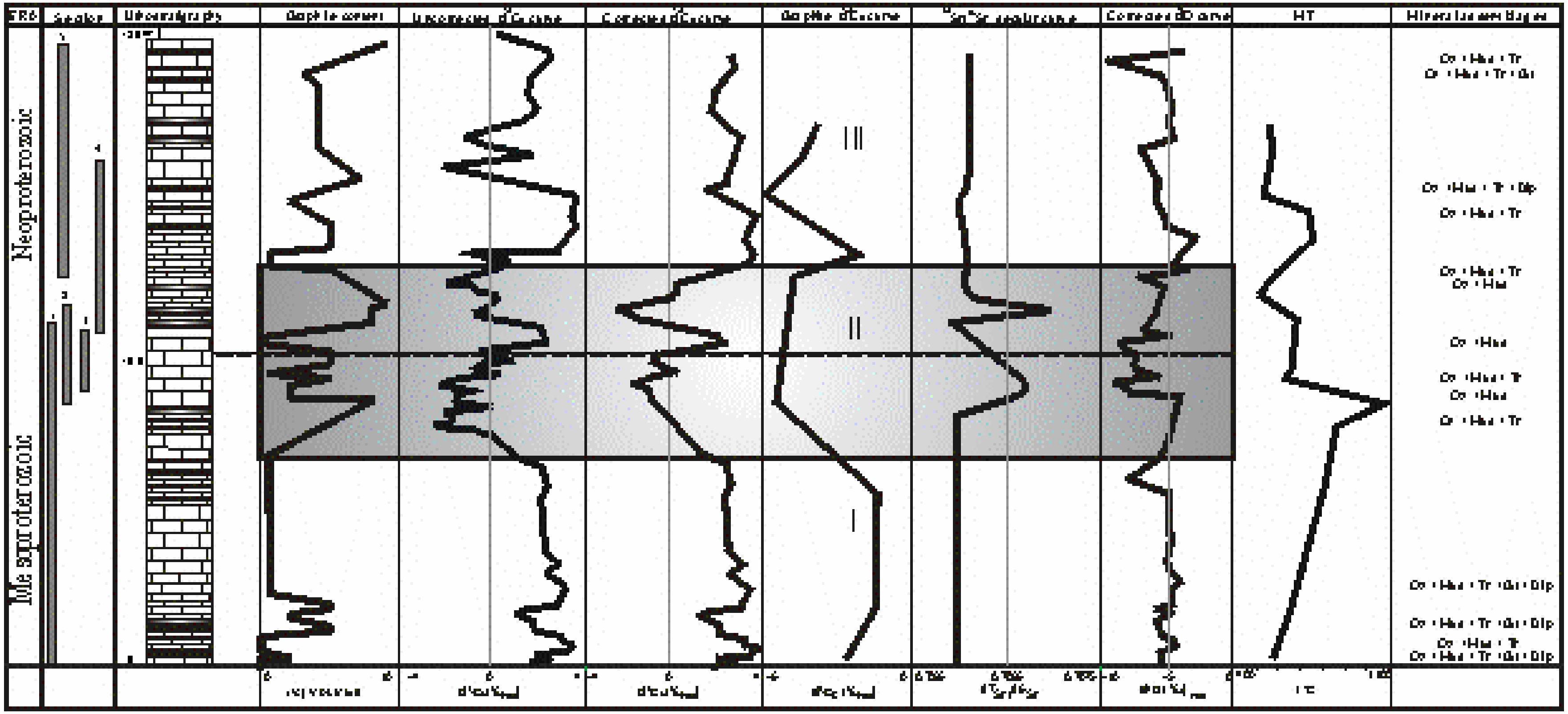


FIGURE 9

CONCLUSÕES

A quimioestratigrafía dos mármores do Complexo São Caetano (CSC), localizados na zona transversal da Província Estrutural da Borborema, mostra variações moderadamente altas nos valores de $\delta^{13}C$ (-2,7 a +3,7‰$_{PDB}$), acompanhadas por variações moderadas nos valores de $^{87}Sr/^{86}Sr$ (entre 0,706 e 0,707). Após comparar as curvas de variação seculares obtidas a partir de isótopos de C e Sr para os mármores estudados com curvas de seqüências de carbonatos sedimentares bem conhecidas a nível mundial (Kah et al., 1999, 2001, Bartley et al., 2001) uma idade Meso-Neoproterozóica (1,1-0,97 Ga) é inferida para a deposição dos protólitos sedimentares dos mármores do CSC.

A idade de sedimentação acima proposta, unida a evidencias regionais tais como a presença de seqüências tipo MORB de 1,05 Ga a oeste do CSC (Bittar, 1998), a ocorrência de possíveis eclogitos a SW do complexo (Santos, 1995) e a presença de granitóides tipo I com T_{DM} de 1,04 Ga, intrudindo-o (Kozuch, 2003), levam a considerar que o Complexo São Caetano ter-se-ia depositado após um evento de rifteamento na Zona Transversal da Província Borborema (entre 1,4 e 1,05 Ga). Este evento de rifteamento é também evidenciado pelos valores levemente negativos de ε_{ND} (-1,84) e T_{DM} de 1,34 Ga, encontrados em granodioritos associados ao Complexo Cabrobró, ao sudeste da área de estudo (Maciço Pernambuco-Alagoas, Osako, et al., 2003) e pelos valores de ε_{ND} entre 0,08 e 5 e idades modelo (T_{DM}) entre 1,4 e 1,04 Ga, encontrados em riolitos intrudindo o CSC; estes últimos apresentando idades U-Pb em zircão de 967± 13 Ma (Kozuch, 2003).

Kozuch (2003), por outro lado, identificou o evento de rifteamento acima citado e um posterior evento de subdução que levou à ocorrência do arco magmático Cariris Velhos a NW do CSC a 0,96 Ga. Evidências para esta subdução são fornecidas pela presença de eclogitos (Santos, 1995) e de granitóides do tipo-I de idade Cariris Velhos. O modelo de Kozuch (2003), no entanto, falha ao não explicar o papel que o CSC, que é certamente contemporâneo ao Riacho Gravata, exerceu na configuração final do arco magmático Cariris Velhos.

Características litológicas da parte siliciclástica do CSC indicam, por outro lado, que este teria-se depositado numa margem continental e em ambiente pelágicos durante um período de nível do mar alto. Esta margem continental teria-se estabelecido ao norte do Cráton São Francisco e de suas supracrustais Meso-Paleoproterozoicas associadas. Convergência de placas oceânica e continental, com subdução associada ao magmatísmo de tipo arco magmático continental (Cariris Velhos), teria ocorrido contemporaneamente à deposição de sua parte mais superior e ao fechamento da bacia oceânica onde este se depositou.

É importante ressaltar que, baseado nos resultados obtidos neste trabalho, o Complexo São Caetano teria desempenhado um papel importante durante o fechamento de uma possível margem continental entre as rochas vulcânicas oceânicas do Riacho-Gravatá e as supracrustais ao leste do CSC, tendo a zona de cisalhamento Afogada da Ingazeira como uma Paleosutura. No entanto, levando em consideração que o CSC foi pouco estudado ate agora, considerações mais precisas sobre a paleogeografía desta área da zona transversal, entre 1,1 e 9,7 Ga, são ainda especulativos. Portanto estudos mais aprofundados, em especial de sua parte siliciclástica, devem ser levados adiante, uma vez que a melhor compreensão da historia geológica do Complexo São Caetano resolveria muitas questões ainda controvertidas. Por enquanto, a idade Meso-Neoproterozoica inferida neste estudo para o CSC indica que a Zona Transversal, na área de estudo, teria permanecido como uma margem continental a noroeste do Crato São Francisco e suas supracrustais, Meso e Paleoproterozóicas, entre pelo menos 1,1 Ga e 0,97 Ga.

Por outro lado, baseados nas variações de isótopos de C nas seções de mármores estudadas, três estágios isotópicos foram observados (I, II, II) que são associados a mudanças na geoquímica da água do mar durante a sedimentação dos protólitos dos mármores e que teriam sido provocadas por eventos tectônicos globais:

a) Estágio isotópico I, no qual valores moderadamente altos de $\delta^{13}C$ (~+3,7$‰_{PDB}$) resultaram de um grande soterramento e posterior seqüestro do carbono orgânico durante o ponto máximo do ciclo orogênico Grenvilliano, que levou ao empobrecimento da água do mar em ^{12}C.

b) Estágio isotópico II, o qual apresenta valores mais flutuantes de $\delta^{13}C$ (-2 a +3$‰_{PDB}$). Esta variabilidade reflete um aumento no aporte de CO_2 rico em ^{12}C associado a um evento de rifteamento global há 1,05 Ga. (valores mais baixo) e o seqüestro de matéria orgânica rica em ^{12}C através de processos de subducção globais, relacionados ‘a formação de arcos magmáticos há ~1,0 Ga a nível global (e.g Cariris Velhos).

C) Estagio isotópico III, com valores de $\delta^{13}C$ em torno de 3,7‰$_{PDB}$ refletiriam novamente um incremento na sedimentação e soterramento da matéria orgânica o qual teria sido incrementado durante a aglutinação do supercontinente Rodinia.

A quimioestratigrafía isótopica de Sr apóia as idéias acima expostas. Valores de $^{87}Sr/^{86}Sr$ ~ 0,706 caracterizam o estágio isotópico I. Estes valores podem representar um grande aporte de material terrígeno continental empobrecido em Sr radiogênico (crosta rica em material juvenil) `as bacias oceânicas no final do Mesoproterozóico. Os valores baixos, no entanto, podem refletir também um evento de rifteamento a nível global entre 1,4- 1,1 Ga. Valores de 0.705 são também registrados em seqüências sedimentares em Canadá e Sibéria (Kah et al., 2001, Bartley et al., 2001) para este período, o que apóia também a idéia de um evento de rifteamento.

Valores mais variáveis de $^{87}Sr/^{86}Sr$ (0,706 a 0,707), por outro lado, caracterizam o estagio isotópico II e podem representar mudanças na atividade tectônica global. Os valores pouco radiogênicos estão associados ao processo de rifteamento global há 1,05 Ga e os mais radiogênicos `a geração de arcos vulcânicos tipo Andes a nível global há 1,0 Ga, respectivamente.

Os valores em torno de 0.706 que caracterizam o estágio isotópico III, representariam a continuidade dos processos de erosão crustal associados à aglutinação de Rodínia e à formação de material juvenil no período 1.05-0.97 Ga.

Finalmente, levando em consideração que a aplicação dos métodos quimioestratigráficos em seqüências de mármores tem sido amplamente criticada, devido às possíveis mudanças da assinatura isotópica durante metamorfismo, uma avaliação de possíveis câmbios na assinatura original dos protólitos dos mármores foi realizada. Caracterizações petrográficas, geoquímicas (elementos maiores e menores) e isotópicas indicaram que: (1) algumas mudanças da assinatura original de isótopos de C ocorreram em algumas mostras de carbonatos do CSC. Estas mudanças foram associadas à presença de grafita; uma difusão entre CH_4 rico em ^{12}C, derivado da grafita, e os carbonatos, é proposta como o mecanismo que gerou dita modificação. (2) As mudanças na assinatura isotópica de C ocorreram, independentemente de mudanças na composição isotópica de O e Sr, sob condições fechadas. Isto é apoiado pela variação pequena dos isótopos de O e Sr, como também pela natureza inalterada dos indicadores de elementos geoquímicos (Sr com media de 1500 ppm, razões de Mn/Sr de 0.006 até 0.140, e razões de Rb/Sr entre 0 e 0.005). (3) O processo de modificação da assinatura isotópica de C nos mármores teria ocorrido sob condições de metamorfismo de baixa pressão – média temperatura. Isto é apoiado por assembléias minerais dos mármores (calcita, quartzo, tremolita, moscovita, diopsidio e granada), as quais indicam temperaturas na faixa de 500-700^{0}C. Um intervalo de temperatura para o metamorfismo entre 514 e 750^{o}C, estimada a partir de termometria de isótopos de C em grafita e calcita coexistentes, apóia esta idéia.

Baseado no acima exposto e nas variações seculares dos valores de $^{87}Sr/^{86}Sr$ e $\delta^{13}C$ é possível afirmar que a composição isotópica dos mármores do Complexo São Caetano reflete a composição isotópica dos seus protólitos sedimentares e que só algumas modificações nos valores de $\delta^{13}C$ ocorreram durante o metamorfismo, independentemente de mudanças na sua química elementar e nos valores de $^{87}Sr/^{86}Sr$. Portanto a composição isotópica destes mármores representa a composição isotópica da água do mar durante a transição Meso-Neoproterozóico.

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