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MINERAL CHARACTERISTICS OF CARBONATES WITH TRACE ELEMENTS. PART 1. CALCITES

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Abstract

Carbonate formation are discussed from all published mineral compositions and the X-ray fluorescence (XRF) analyses with contents of carbon and other foreign elements. New formation of metamorphic calcite minerals are discussed by these elements with the XRF data of present sea-shells, transparent calcite crystal and aragonite, and coloured calcites (grey, red and green) and marble-stones of European and Middle-East countries used for wall-stones. Mineral characteristics of these foreign elements of Na, Mg, Al, Si, P, S, Cl, K and Fe, replaced in Ca and C, in calcite-carbonates are considered to be new indicator of these formations at their circumstances (such as sea-floor or sea-surface, rocks of plate-tectonics or meteoritic metamorphism at the crustal rocks).

Key words: carbonates, calcite, marble-stones, carbon, trace elements, XRF analyses

Introduction

Carbonate minerals are considered to be sedimentary rocks by the following reaction:

1. Fossil (Ca) relicts with carbonate ion (CO_2) by chemical reaction during sedimentation.

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2. Chemical re-crystallization after original carbonates, such as limestone cave formation by underground water (as stalactite and stalagmite and staracmite) (Miura, 2006 a,b, 2007a,b, 2008a,b). Recently it was pointed out that there is a third way of calcite carbonates formation – throughout a metamorphic process (French, 1998; Miura, 2007a,b, 2008a,b; Miura and Tanosaki, 2009).

The main purpose of the present paper is to make clear the main mineral composition of carbonates from published and collected minerals with minor elements as metamorphic formation process.

Mineral compositions with carbon and other elements

From published mineral compositions (University of Sheffield, 2006; Miura, 2008 a,b), most of the carbon (C) element in all minerals (210 C-bearing minerals with more than 5%C) is combined (61% in all carbon-bearing minerals) as three (66 minerals, such as $CaCO_3$) or four (63 minerals, such as dolomite) elements in each mineral composition (fig. 1). This indicates that carbon element forms almost all mineral composition together with three or four other elements on the Earth.

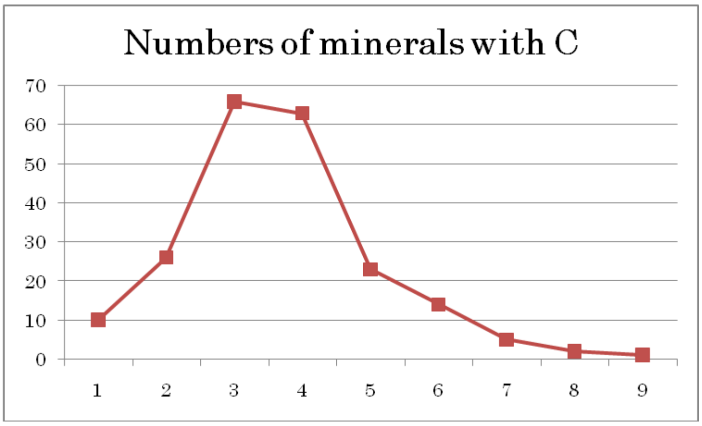


Fig. 1 Numbers of carbon-bearing minerals on the Earth (University of Sheffield, 2008a,b)

Carbon-bearing mineral compositions with three elements

From published mineral compositions (University of Sheffield, 2006; Miura, 2008 a,b), carbon-bearing minerals with three other elements form 180 minerals with 24 type of elements involved in the combination (except C) as shown in figure 2. This indicates that carbon C is easily combined with oxygen O (35% in 180 minerals) to form oxides, whereas carbon is bonded to hydrogen H (24% in 180 minerals). Carbon is the main key-element to form mineral composition with O and H element (59% in three element combination) among gas (atmosphere) and liquid (water) on the cyclic Earth.

Figure 3 indicates C-bearing minerals with three elements (except H and O; 73 minerals with 22 elements) with Ca as the main element (15 minerals and 21% in 73 minerals), as well as with Mg-Ca-Na elements (28 minerals as 55% in 73 minerals). This shows that carbonates with Ca and Mg are easily formed not only by chemical sedimentation but also by metamorphic reaction.

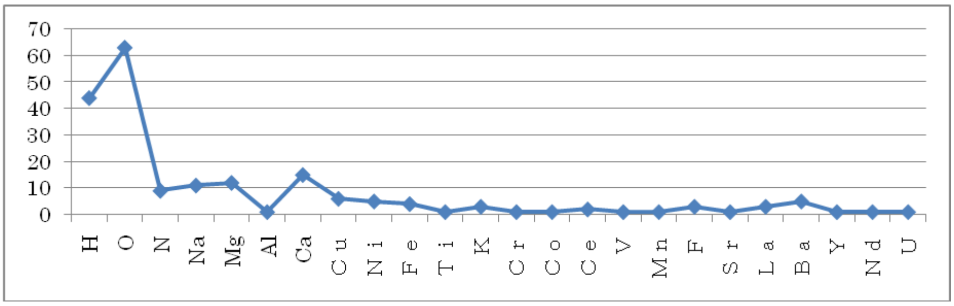


Fig. 2 Numbers of carbon-bearing minerals with three out of 24 elements on Earth (University of Sheffield, 2006)

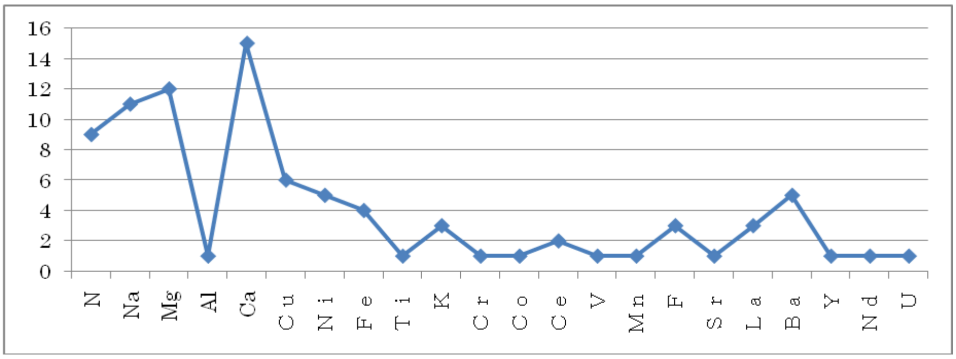


Fig. 3 Numbers of carbon-bearing minerals selected with three elements on the Earth (University of Sheffield, 2006)

Carbon-bearing mineral compositions with four elements

Carbon-bearing minerals with four other elements out of 28 involved in combination (except C) form 252 minerals as shown in figure 4 (data from University of Sheffield, 2006). This indicates that carbon is easily combined with oxygen O (25% in 252 minerals) to form oxides, whereas carbon is bonded to hydrogen H (17% in 252 minerals). Carbon is still the main key-element to form mineral composition with O and H element (42% in four element combination) among gas (atmosphere) and liquid (water) on the cyclic Earth. Percentages of carbon-bearing minerals with four elements are lower than that of minerals with three elements (figures 2, 3, 4, 5). This indicates that carbon element is easily combined with many other elements as minor contents during the main carbonate formation. This result could elucidate the carbonate formation from mixed minor element in produced circumstance.

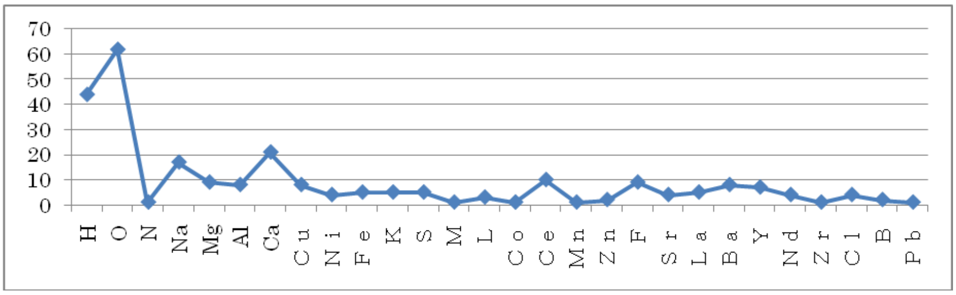


Fig. 4 Numbers of carbon-bearing minerals with four elements out of 28 on the Earth (University of Sheffield, 2006)

Figure 5 indicates C-bearing minerals (except H and O; 146 minerals with 26 elements) with Ca as the main element in the chemical formula (21 minerals and 14% in 146 minerals), as well as with Mg-Ca-Na elements (47 minerals as 32% in 146 minerals). This also shows that carbonates with Ca and Mg in C-bearing minerals with four elements are formed not only by chemical sedimentation but also by metamorphic processes.

Published standard compositions of calcite and dolomite carbonates

Six standard calcites and four dolomites published by Govindaraju (1994) are shown in figure 6 as follows:

1. It is difficult to obtain chemical pure samples of calcite and dolomite without any contamination.

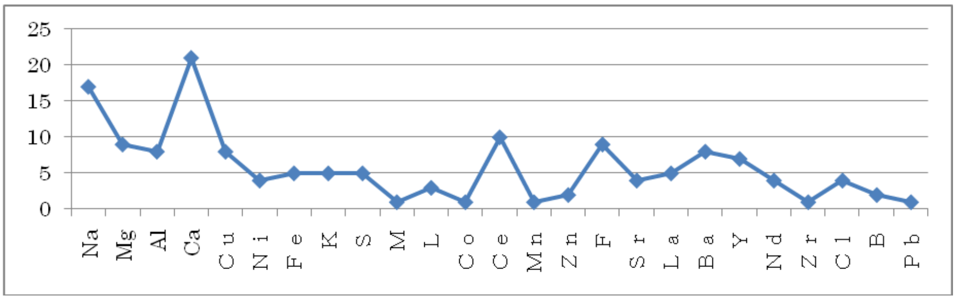


Fig. 5 Numbers of carbon-bearing minerals selected with four elements on the Earth (University of Sheffield, 2006)

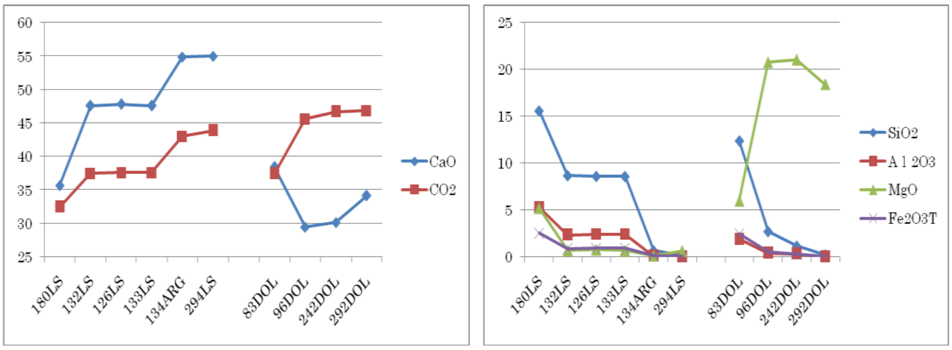


Fig. 6 Major chemical compositions of standard calcite and dolomite published by Govindaraju (1994)

2. Calcite with high Ca and less C (than dolomite) contains anions of Si, Al, Mg and Fe as minor contents.

3. Dolomite with high C and less Ca (than calcite) contains also Si and Fe, as well as Ca and Mg, where characteristic of dolomite composition is much carbon content than calcite.

This indicates that standard carbonates without any contaminations are difficult to find in the world, whereas almost all carbonates contain minor elements of Si, Al and Fe (except Ca and Mg).

It requires to be compared with any differences between sea-fossil carbonates and minerals in the crust carbonate-rocks.

XRF measurements of sea shells

In order to analyze carbonate samples with C-bearing compositions, an XRF (X-ray fluorescence) device (the Rigaku SQX model by powdered bulk-sample) has been used to obtain light elements as C with EDX analyzer (by ZAF calculation) (Miura, 2007a,b, 2008a,b; Miura and Tanosaki, 2009).

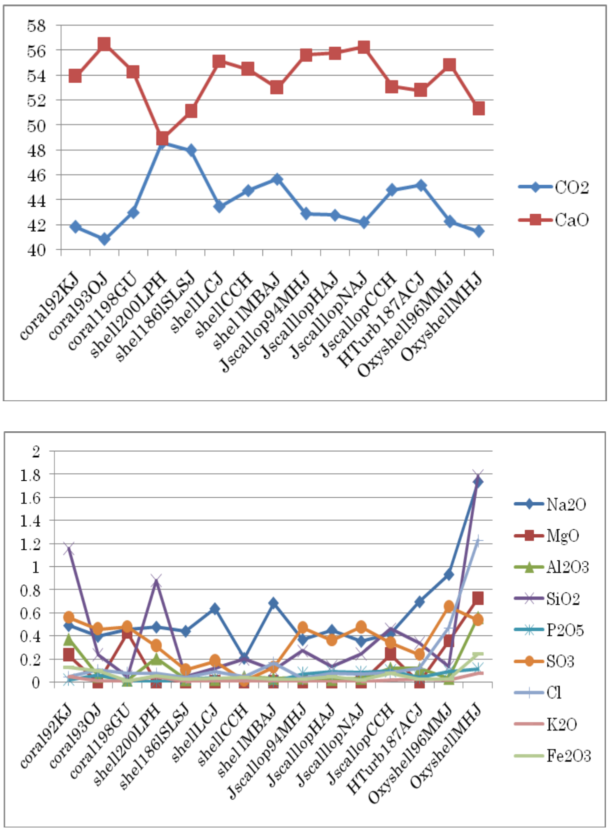


Fig. 7 Major chemical compositions of calcite carbonates from 15 present sea-shells analyzed by the XRF instrument

Figure 7 shows major oxides compositions of 15 samples of different sea-shells, which indicate as follows:

1. It is difficult to obtain pure chemical samples of calcite in sea-shells, which are formed by secondary crystallization (relatively static condition) with individual life-shapes.

2. Significant feature of sea-shell is that Na, Cl, Mg and S are the main ions in calcite formed from sea water composition, which is considered to be major chemical differences against calcite formed from crustal rocks.

3. Ca contents are always deficient than pure calcite composition due to replacement by Si, Na, Cl, S and P (and minor Mg, Al, K and Fe), though carbon contents are rich in sea-shells on the sea-floor but poor in surface sea-water. Chemical compositions of calcite in sea-shells are considered to be related with location and circumstances in the sea.

This indicates that chemical compositions of present sea-shells (before fossils) are not pure calcite carbonate compositions but those related with sea water (especially including Na, Cl, Mg and S) . Carbon contents are changed at locations of sea-shells, that is on the sea-floor rocks or floating near surface, which are considered to be strong indicators of present Ca-carbonates (including calcite) formed at sea-water as follows.

Sea-shells → (1) living on the sea-floor rock: C, Na. Cl, P, S rich composition
(2) floating near sea surfaces: Na, Cl, Mg and S rich composition.

XRF measurements of calcite-limestones

Calcite with various shape crystal faces and colours are analyzed by the same way with the XRF instrument with the EDX analyzer (Miura, 2008a,b; Miura and Tanosaki, 2009).

Figure 8 shows major oxides compositions of 5 samples with clear crystal shapes as follows:

1. Transparent calcite crystal has the least foreign elements of all crystals or trace amounts of P.

2. Coloured calcites show deficient CO_2 than transparent crystal, where minor Si, Mg and Al contents are obtained for green calcite, and where minor contents of S, Mg and Si (Al) are analyzed for orange calcite.

3. Aragonite (as high pressure type) contains deficient CO_2 than transparent crystal, and the similar minor elements with coloured calcite (as low pressure type) , especially anomalous minor S element.

4. Dolomite-calcite show significant foreign elements of Fe and Cl (with minor Si and Al), together with standard dolomite composition.

Carbon contents of calcite are relatively lower due to foreign elements of Si, Al, Mg, P, S, Cl and Fe, whereas Ca contents are relatively higher than normal calcite.

calcite → (1) few foreign elements for transparent crystal (except P) and aragonite.

(2) minor foreign elements for coloured calcites with Na, Mg, Al, Si, P, S, Cl and Fe.

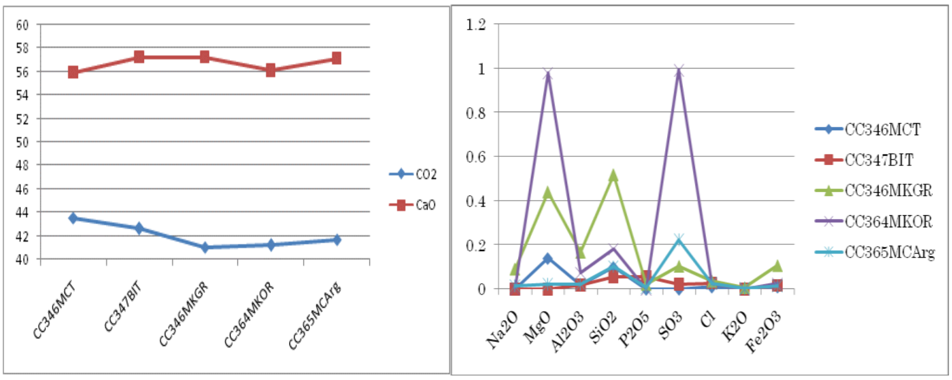


Fig. 8 Major chemical compositions of calcite and aragonite from 5 samples analyzed by the XRF instrument

XRF measurements of European and Middle-East marble-stones

Marble-stones of 27 European and 6 Middle-East countries (used for wall-stones) were analyzed with the XRF with EDX devices, the result being summarized as follows (fig. 9; Miura and Tanosaki, 2009).

1. The samples indicate deficient CaO and CO_2 contents due to foreign elements of Si, Mg, Al, S and Fe;

2. Significant amounts of Mg, Al, Si, P and K are obtained at Italian samples in this study, which is considered to be mixing with crustal rocks mainly by plate-tectonic movements (as metamorphic formation).

3. Characteristic amounts of Fe and S with minor Na and Cl are found in Spanish samples in this study, which is considered to be mixing with crustal rocks by meteoritic flux in the sea-water condition (as metamorphic formation).

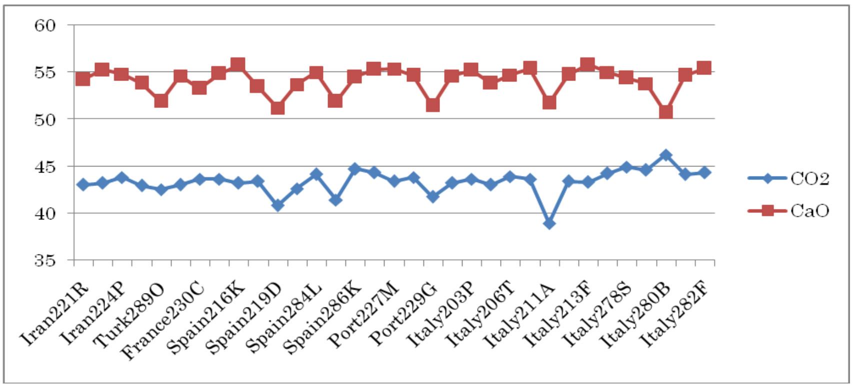
Other carbonates and calcite compositions with the XRF analyses

The same chemical compositions of carbonates and calcite compositions with the XRF data are discussed on Japanese and world-wide samples at the next papers.

Conclusion

The present results are summarized as follows:

1. Chemical compositions of calcite – bearing carbonates with carbon contents were investigated by XRF in order to characterize formations of fossil sedimentations, chemical re-crystallization and metamorphic calcite-carbonates.



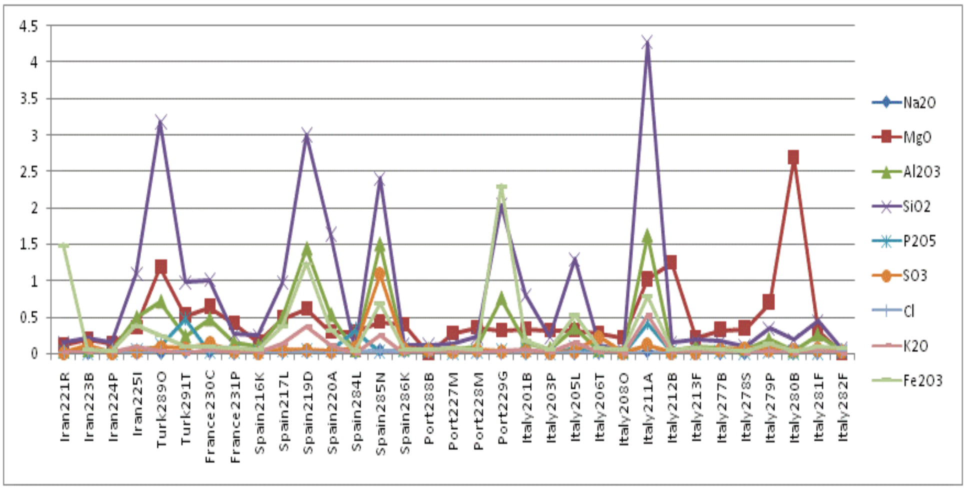


Fig. 9 Major chemical compositions of 33 European and Middle-East marble-stones analyzed by the XRF instrument

2. From published compositions of carbon-bearing minerals, carbon is mainly combined with three or four elements especially with O and Ca (or Mg) to form carbonates by various formations on the Earth.

3. The previous published standard calcite carbonates contains foreign elements of Al, Si, Mg and Fe, though there are no relation with other foreign elements by various types of formations.

4. The XRF data of present sea-shells (before fossils) are not pure calcite carbonate compositions but those related with sea water (especially including Na, Cl, Mg and S) . Carbon contents of sea-shells are characteristic indicators of locations of sea-floor rocks or floating near surface.

5. The XRF data of transparent calcite crystal and aragonite show few trace elements (except P) , whereas coloured calcites (grey, red and green) with relatively deficient carbon contain minor trace elements of Na, Mg, Al, Si, P, S, Cl and Fe.

6. The XRF data of marble-stones of 27 European and 6 Middle-East countries (used for wall-stones) indicate that Italian samples contain Mg, Al, Si, P and K mixed with crustal rocks mainly by plate-tectonic metamorphism, and that Spanish samples contain Fe and S with minor Na and Cl mixing with crustal rocks by meteoritic metamorphism in the sea-water condition.

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