BAGHOUSE FINES OF CORALINE LIMESTONE OR FOSSIL CORAL WITH CALCIUM CARBONATE - RESULTS OF PRELIMINAR RESEARCH

ID 080   **Željko POGAČNIK[1], Miha ANDREJAŠIČ[2], Igor ŠTERN[2], Mateja GALEŽ[3], Simona MURKO[4]**

[1] Salonit Anhovo, Building Materials, Joint-Stock Co, Deskle, SLOVENIA
[2] Jozef Stefan Institute, Department of Biochemistry and Molecular Biology, Ljubljana, SLOVENIA
[3] The Laboratory For Stone and Aggregates, Slovenian National Building and Civil Engineering Institute, Ljubljana, SLOVENIA.
[4] Jozef Stefan Institute, Department of Environmental Sciences Ljubljana, SLOVENIA.
zeljko.pogacnik@salonit.si

ABSTRACT

Osteoporosis is one of the more common disorders in the developed countries (Zethraeus, N., e tal., 2007). Despite the known pathological condition an effective treatment of the disorder other than calcium administration is still unknown. Whereas the drugs for diminishing the negative effects of the disorder in the pharmaceutical industry and in the healthcare are subjected to rigorose efficiency analyses, no such can be said for the food additives which are obtained on the free market. In such food additives which are offered to help inhibiting and diminishing the effects of osteoporosis, calcium is bound in fossil chorals and in calcium carbonate.

Is there a possibility that the commercial food addictives contain powdered reef limestone also known as baghouse limestone finess, which is being taken into bag filters at dedusting processes, instead of the questionable decalcinated fossil coral and calcium carbonate? And even so, how do they – from the point of physical and chemical properties – differ from the varieties of calcium binding limestone from the success promissing food additives?

Key words: corals, limestone finess, baghouse, osteoporosis, bone resorption, bone metabolism.

INTRODUCTION

Some diagenetically changed sedimental rocks from some locations in the Indian ocean show affinities with the recent reef formations (Wigley, 1973). From this, a scenario was predicted, taking into account some restraints regarding results interpretation (Buchardt e tal., 1981), so that it would be possible to use such mineral materials in food industry. The standards (SIST EN 12620:2002 with appendixes) for the concrete aggregates demand limited amount of alkalies (bases), organic and other components. From this it can be concluded that the most suitable are carbonate rocks.

We proposed pleistocenic or younger deposits as a hypothetical geografical source of a high quality mineral raw material. Based on this, the geographical position, geological factors and according to some literature sources we analysed:

1. alimentary products that contain – according to the declaration – fossil corals and calcium carbonate;
2. recent corals from the Indian ocean and the Mediterranian sea;
3. fossil jurrasic reef organisms (petrified corals, algae and stromatophores);
4. the mineral raw material from some quarries, that does not etymologically belong to a coral reef environment.

The intention of these analyses was to compare some characteristics and calcium content of food products/additives placed on the market with dust particles regarded as waste material and produced daily in different quarries. Due to a constantly higher percentage of osteoporosis patients (reviewed in Zethraeus et al., 2007), the calcium food additives as the only preventive treatment of the disease are a highly profitable product.

Osteoporosis is a disease characterised by the loss of the bone mass. The cause(s) of calcium resorption from the bone tissue and the imbalance of calcium in the body is(are) unknown. Calcium is very important in different processes in the body; for example: it is a co-factor in enzymatic reactions and plays a key role in signal transduction in the nervous system. Furthrmore, it precipitates if co-locallised with phospate ions, its concentration in the body fluids as well as in the cellular cytoplasm is strictly controlled. Calcium is predominantly stored in bones. The metabolism of calcium deposition in and resorption from the bone tissue is controlled mainly by hormones, insulin, vitamin D3 and mechanical pressure. Clinical studies have shown that treatment with vitamin D3, calcium, bisphospates reduce risk of fructure (Zethraeus et al., 2007).

Explanation of some expressions

Before the introduction into the experimental work, some expressions should be defined that were encountered and that lead to the working hypothesis in the first place.

Coral calcium definition in the Slovenian alimentary products

The definition of the calcium content in alimentary products is mainly expressed as: »the product contains calcium carbonate, coral powder that cointains calcium and magnesium, fossil coral powder, calcium carbonate, magnesium oxide or magnesium stearate, vitamin D3, gelatine, calcium citrate, calcium phosphate, sillicium dioxide, microcrystallinic cellulose.« *Coral calcium is connected to organisms, whose skeletons are constituted of organic minerals in the sea.*

Expressions »fossil« and »fossil coral«

Fossils are remains of plants and animals that lived in different geological periods and that hardened – were converted into rock. Rock is a natural substance, composed of grains of one or more different minerals or of different fragments of other rocks. A fossil coral is rock made in geological processes and composed of minerals and compounds with a defined, characteristic chemical and ordered crystal structure.

Living environments of corals and sea reef organisms

A sea reef represents a sequence of generations of settling the organisms and as such it is a very complicated ecosystem (Figure 1).
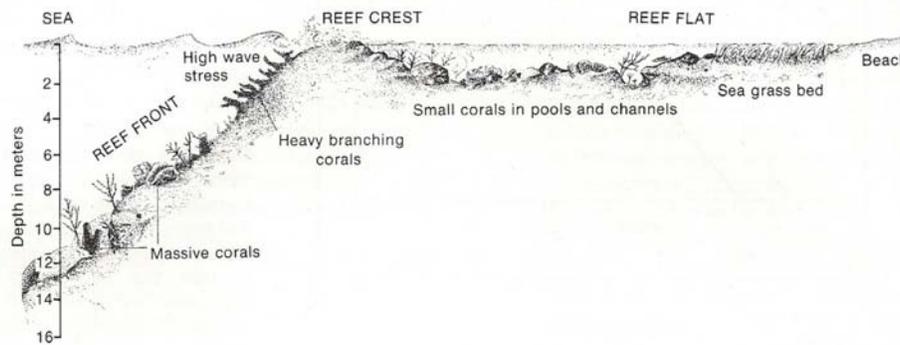
Figure 1.: A cross section of a fringing reef (Barnes and Rupert, 1993).

The coral zonation depends on the possibility of inhabiting the local environment and on the type of the sediment. In this way, it is different for different reefs. (difference between the Carribean and the Indo-Pacific coral reefs), which differ according to the topography and the algae colonies overlay on the sediment. Contemporary reefs can be divided into fringing, barrier and atol reefs and are successively linked between each other. The fringing reefs are linked to shorelines, whereas the barrier reefs are predominantly found in off-shore environments. The atol reefs have mostly a horse-shoe shape and are oriented towards the strongest winds, which consequently affects the food influx. In the inside of the atols a patch reef can be formed. After the pleistocene sea level change the corals populated the anomal typography. For this reason, it is impossible to reconstruct the fossil reefs (the Mesosoic and the Jurrasic ones), which were spread all over Europe, from the recent ones (Turnšek, 1997). The recent reefs are connected to the tropical region and grow best in the Indo-pacific region where over 700 species were determined. Structurally resistant and massive reefs form Scleractiniae, where the endosymbiotic organisms and green algae play an important role as carbonate producers. In this way, they help building and strengthening the reef (Figure 2.).
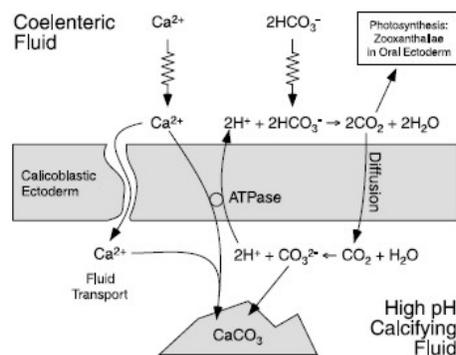
Figure 2.: A schematic presentation of a calcification system (Sinclar and Risk, 2006).

On the microscopic level, the endosymbiotic photosynthetic unicellular organisms that transport food – zooxanthellae (which are inherited or acquired by a coral). The endosymbiotic algae – dinoflagelatae – live in the gastrodermal zone. The coral gives the endosymbiont organism a space to dwell as well as substances, used by the latter for photosynthesis: CO_2, nitrates, phosphates and the organic compounds which represent the waste products in the coral metabolism. In exchange, the coral gains oxygen, calcium carbonate and organic products of the photosynthesis, used for biosynthesis.

Calcium carbonate and the sedimentary rocks

Calcium carbonate is a compound with an ordered crystal structure and an empirical formula $CaCO_3$. In carbonate reefs, the carbonate metabolism ranges from 3 to 5 kg/m^2, which demands a high specialisation of the reef fauna. In the Britomart reef region on the northern shore of Australia a recent reef was found which had been formed on a Holocene ancestor (Johnson and Cuf, 1984). In that area the following structural lithotypes of the sediment rocks were found (Dunham, 1962): the coral boundstone, the coral framestone formations and the coral rudstone firmation (slime-based).

Hohenegger and colleagues (1999) published a study on the habitat of the larger foraminiferae from the upper parts of a reef on an island belonging to the Okinawa isles in which two different kinds of sediments were described till the deepness of 60 m.

Definition of the Baghouse limestone finess

In the case of surface mining in dry – arid – climate conditions it is necessary to use dust-off systems (cyclons and baghouses). The quality of the captured dust particles depends on the raw material quality, on the raw material manufacturing technology and on the technology of dust capturing. Taking into account the life span and the type of a quarry, the raw material composition remains more or less unchanged.

Table 1.: Granulometric relationship of dust particles from ten different mineral raw material mines according to the type of the matrix raw material (Wood and Marek, 1993).

Rock Type	Percent Passing Sieve Size							
	.075 mm	.05 mm	.03 mm	.02 mm	.01 mm	.005 mm	.003 mm	.001 mm
Limestone	100	96	82	67	43	23	14	4
Granite	100	98	95	84	53	29	17	7
Granite	100	89	43	18	8	3	2	1
Granite	100	94	69	51	32	16	10	4
Granite	100	100	99	96	78	49	32	12
Trap Rock	100	98	89	76	48	24	14	5
Limestone	100	96	93	89	74	46	31	12
Limestone	100	95	66	37	11	7	5	3
Limestone	100	95	80	62	43	27	18	7
Quartz	100	100	100	100	99	93	75	10

CHOICE OF MATERIAL

The captured dust particles come from locations where rock is used as technical stone and as raw material for calcium lime. These samples we termed V1, V2 and V3. The chosen

food products that can be purchased without a medical prescription in Slovenian pharmacies were labelled from V9 to V12. As fossil coral samples (jurrasic period, Turnšek, 1997), we chose *Ellipsactinia* (sample V15), an alga *Solenopora* (sample V13) and a coral *Calamophyllopsis flabellum* (sample V14) that belongs to the upper oxfordian-kimmeridgian coral assemblages of Dinaric Carbonate platform (Outer barrier reef). The recent corals: Indian sea corals *Montastrea cladocora* (sample V16), the Maditerranean coral, *Cladocora* (sample V17), octocoralia *Tubipora sp.* (sample V18) and a bryozoan sample (sample V19).

ANALYTICAL TECHNIQUES

To determine the size-class of different food products, the laser granulometric analysis on Masrter Syser (Malvern Instruments) was used. Recording conditions: the samples were measured in the air at the wavelenght of 632.8 nm. A Malvern Instrumnts sofware was used for statistical calculations for determining the particle distribution in samples.

To determine thermal decay of the mineral structures and to determine temperature parameters of decarbonatisation based on the literature data (Mackenzie, 1957, Ramachandran, 1969, Taylor, 1997) the STD 2960 Simultaneus DTA-TGA analyzer was used. Measurments were carried out using a standard protocol: 10 °C/min - 1200 °C, temperature gradient step 10 °C/min. Thermometric analyses were prformed using a computer software programme »Universal Analysis for Windows 95/98/NT, Ed. 2.5H«. We followed the parameters listed in the Table 1.:

Table 1.: The traing parameters used in the thermal analyses (Mackenzie, 1957 and Buchi, 1980).

	Explanation
T_1	Temperature where the instrument detected the beginning of a reaction = T_i
T_2	Temperature at wich the reaction is finished : $T_{offset} = T_f$
t_1	Time in which the thermal process initiated at linear heating
t_2	Time when the thermal process finished at linear heating.
T_{onset}	Temperature when the chemical rection (decay) takes is initiated
T_{max}	Temperature maximum of an initiated process
m	Mass changes during reaction

The point element analysis was carried out with a raster electron microscopy and an electronic dispersion spectrometre JEOL LN 5200 at the working voltage of 20 kV and pressure from 12 to 18 Pa.

Food supplement samples of 300 mg were washed with acetone three times with 500 μL and dried on SpeedVac. The same protocol was used when washing with water prior to resolving in Aqua Regia. All samples were prepared by resolving 10 mg of crushed sample in 1 mL of freshly prepared Aqua Regia and diluted with Milli-Q water to 10 mL. 100 μL of each sample was transferred into a measuring container and diluted to 10 mL. The blank was prepared in same way.

All measurements were carried out on the inductively coupled plasma mass spectrometer Agilent 7500ce (Tokyo, Japan). AN auto sampler (ASX 500) and sample introduction kit consisting of a Babington nebulizer and a Scott-type glass spray chamber were employed to transport the analyses into the plasma of the ICP-MS. Details of the ICP-MS operating conditions and the data acquisition parameters are summarized in the table 2.

Tabela 2.: Operating conditions of ICP – MS analaysis.

Parameters	Operating conditions
RF power	1500 W
Make up gas	0,13 L/min
Coolant Ar flow`	15 L/min
Torch-H	0,6 mm
Torch-V	0,3 mm
Sample cone	Ni
Skimmer cone	Ni
SMPL	8 mm
Nebulizer pump	0,1 rps

Before analysis, the ICP-MS measuring conditions were optimized using a solution containing Li, Mg, Co, Y, Ce and Tl at a concentration of 1 μg/L.
To prepare the standard and the blank solutions, high purity Milli-Q water obtained with an ELGA purification system (resistivity less than 18 MΩ/cm) was used.
Calibrating and reference solution was Multi Element Standard Solution 4 (Merck, Germany) at 1000 mg/L containing Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl and Zn.

RESULTS

Beam reflections as a consequence of dissipation on particles under different angles were detected, measured and transformed into numerical values by an »element detector«. The numerical values were transformed into a suitable form by a suitable optical model and a mathematical procedure. The output was a relationship between the total volume of a discrete size-class volume numbers and the intensity of the scattered light (Table 3.).

Table 3.: Size distribution of the particles in food products.

Sample	Volume percentage (%) under 50 μm
V9	91,00
V10	100,00
V11	92,67
V12	89,87

Thermal analysis represent a number of methods by which sample features were constantly observed at controlled temperature interval changes. The mineral composition and rock reactivity were observed by thermogravimeric TG analyses (Macenzie, 1957, Bucchi, 1980,

Taylor, 1997). The calcium percentage in a rock was determined by IPC-MS analyses (Table 3.).

Table 3.: The carbonate and trace components percentage in the samples (thermal reactivity of a mineral- α -factor – defined as $dT/dt = (T_2 - T_1)/(t_2 - t_1)$.

Sample	T_1	T_2	t_1	t_2	Δm	$CaCO_3$	T_0	T_{max}	Sr	Mg	Ba	Ca	Sr/Ca	α
	(°C)		(min)		(%)	(%)	(°C)	(°C)	Qualitative estimation					(°)
DTA – TG analysis									ICP – MS analysis					
V1	601,90	840,40	58,53	82,47	43,46	98,77	697,88	800,24	0,00	0,00	0,00	13,90	0,00	84,3107
V2	620,10	842,30	60,77	83,08	42,79	97,25	695,83	805,61	0,00	0,00	0,00	12,90	0,00	84,3092
V3	628,20	838,70	61,14	82,27	41,78	94,95	700,77	797,64	0,00	0,00	0,00	12,90	0,00	84,3106
V9	582,90	815,30	57,18	80,44	32,60	74,09	683,23	775,58	0,00	0,90	0,00	9,90	0,00	84,3273
V10	573,00	827,50	56,20	81,68	43,57	99,02	683,29	781,92	2,70	0,00	0,60	12,90	0,21	84,3255
V11	620,50	845,50	60,48	82,96	42,62	96,86	698,01	804,37	0,40	0,00	0,10	12,90	0,03	84,3372
V12	625,40	829,40	61,31	81,71	40,91	92,98	682,11	783,52	30,60	0,00	0,20	11,90	2,57	84,3322
V13	648,60	826,10	63,61	81,63	43,12	92,98	694,41	787,25	0,00	0,00	0,00	12,90	0,00	84,2458
V14	622,10	839,50	61,23	82,99	43,87	92,98	700,27	797,95	0,00	0,00	0,00	13,90	0,00	84,3269
V15	643,70	834,30	62,65	81,73	43,20	92,98	704,03	797,93	0,00	0,00	0,00	12,90	0,00	84,3262
V16	598,50	818,90	58,68	80,75	41,45	94,20	680,01	782,74	71,60	0,02	0,60	13,90	5,15	84,3244
V17	588,30	820,10	57,55	80,78	40,03	90,98	685,04	774,16	62,60	0,00	0,10	12,90	4,85	84,3199
V18	610,50	804,70	60,04	79,45	41,60	94,55	684,63	772,03	21,60	0,00	0,00	12,90	1,67	84,3351
V19	593,60	805,40	58,31	79,49	41,66	94,68	673,02	765,79	67,60	0,00	0,00	15,90	4,25	84,3322

Analyses, performed using a raster microscope showed presence of sulphur (figures 3., 4. and 5.) that it is probably bound to a decaying or a diagenetically altered organic component of corals – the dead polyp.
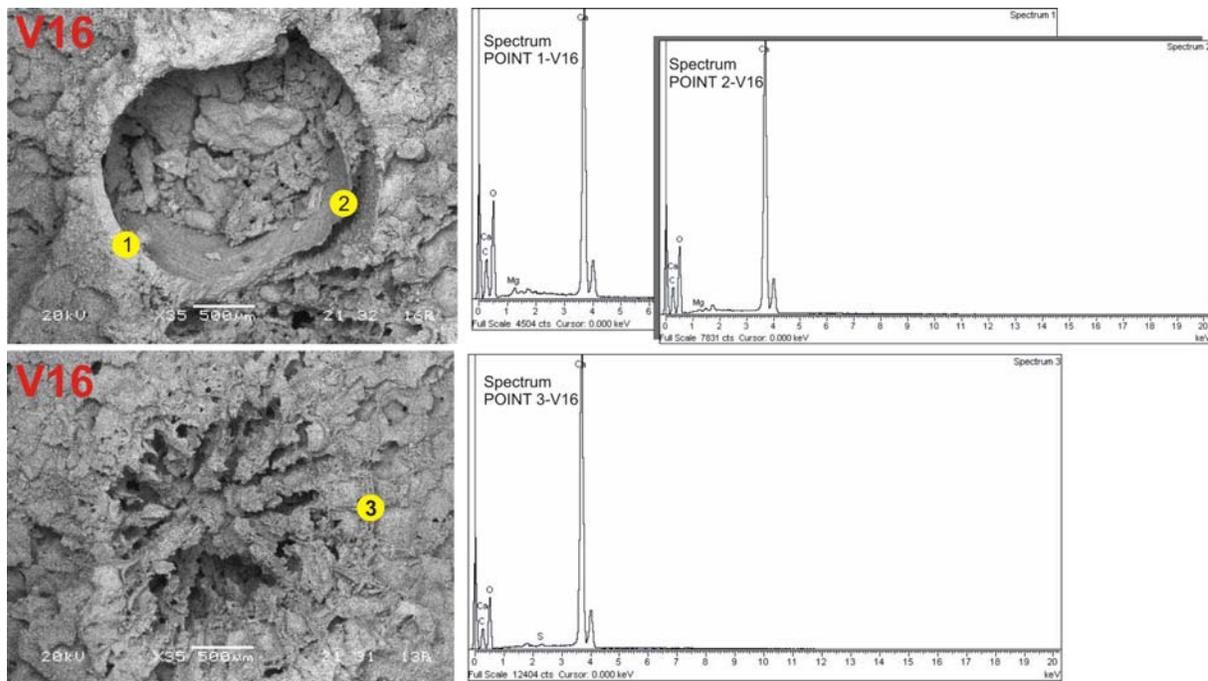
Figure 3.: Point element analysis of some structural elements in *Montastrea Cladocora* (from W Australian reef) (sample V16).
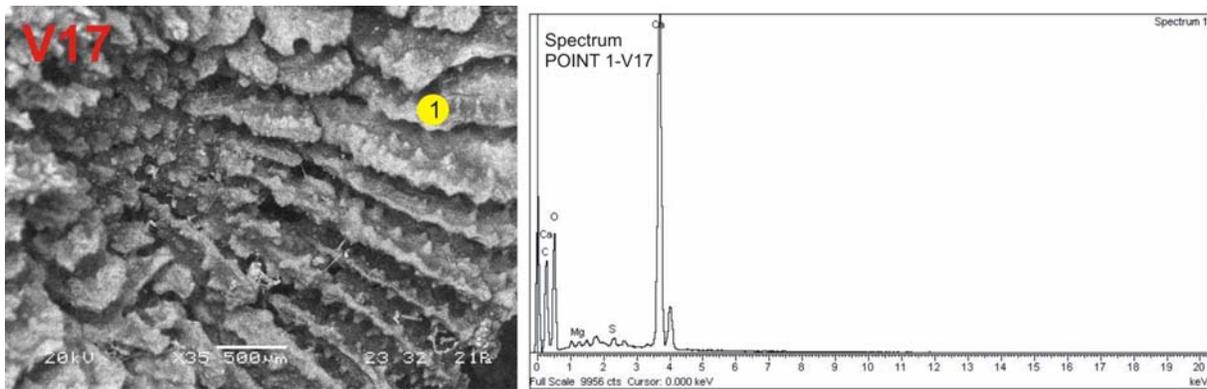
Figure 4.: Point element analysis of the sample V17 - corals *Cladocora* from the Piran bay.
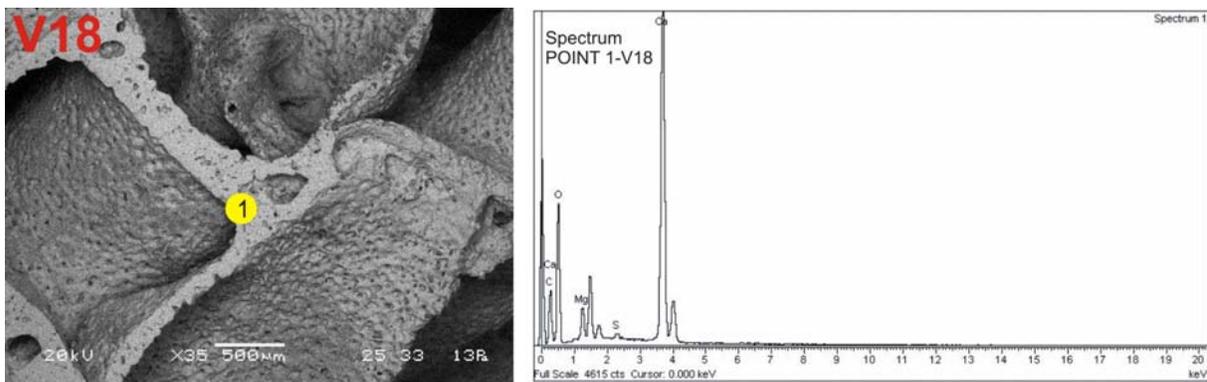
Figure 5.: The point analysis of the sample V18 (Octocoralia, *Tubipora* sp.).

DISCUSSION

From the presented results it can be concluded that the calcium carbonate portion (in the form of constituent or as sedimentary rock) in the insoluble pellet of the food products is above 90 % (w/w) with the exception of the sample V9 where it was 74 %. Despite the difference the carbonate portion exceeds the granulometric arrangement borderline of 12 % (table 4.). Thus, it can be concluded that the finess of the carbonate material cannot disprove the theory of using the dust particles from quarries production.

Interestingly, Sr^{2+} values differed indifferent samples. Strontium ion can be found in human tissues, also in bones. It was shown that strontium ion can replace calcium ions and that they do not effect each other when tested in certain cell types (Olson and Cazort, 1969).

It has turned out that only the sample V12 exhibits a similar Sr/Ca ratio as it is in the recent corals. In all other samples, the ration has much lower values. The sample V9 has a very similar Sr/Ca ratio to the ratio in both, (a) the high carbonate technical stone used for lime production and (b) the reef limestone from the Jurrasic and cretaceous periods. These ratios are connected to the diagenesis level to which rocks was exposed in their geological history.

The early diagenesis changes of aragonite, which is found in coral skeletons, can be traced in the living and in the fossil post-pleistocene species of scleractinian colonies on the microstructural level (Perrin, 2004). The skeletons are biominalised structures, made of the inorganic aragonite and organ skeletons. The scletactinian corals skeletons is composed of two distinct structural units, the calcination centre and the fibres.

The first part of diagenesis in living colonies starts already in the older parts, possibly some years after the polyp's death, when there is no change of the living environment. The constant environment conditions were proven by measuring sulphur amounts in samples. According to the literature (Buchardt and Weiner, 1981; Perrin, 2004), the diagenesis can be observed in the sintaxial aragonite cement structures that can be found in the inner aragonite coral walls and goes from the outside into the inside. The process is going on on the structure level, whereas the mineralogy remains the same and can be hence difficult to detect by thermal analysis. Buchardt and Weiner (1981) proved that the Mg/Ca ratio (compared to the calcite ratio) is a good inorganic parameter of the diagenetic processes in rocks; aragonite is thermodynamically less stable than calcite, therefore it is harder to identify it in older rocks. And when if detected, it can probably be assigned to the diagenetic processes.

It is hard to trace the sintaxial aragonite type in the connective matrix in the fossil rocks that were exposed to meteoric precipitations. The aragonite percentage drops to one half of the original value as a consequence of the meteoric diagenesis (Smith, 2004), which was found by Amiel and co-workers (1973) when analysing the Bermuda recent corals. There, Sr^{2+} replaces Ca^{2+} in the aragonite crystal structure. On the other hand, the change of aragonite into calcite takes place predominantly under the subaerean conditions where the Sr^{2+} amount drops. Wigley (1973) reports that the Sr^{2+} amount is proportional to the Sr^{2+}/Ca^{2+} ratio in the solution from which calcite was formed, and the distribution coefficient of Sr^{2+} in calcite. It is possible, though, that Sr^{2+} amount could be controlled by coral algae.

Thus, it can be concluded that the Sr^{2+} amount (or the relative absense of Mg^{2+}) in the samples is a consequence of diagenetic processes and as such it is a good indicator of the diagenetic processes and/or the environment to which rocks are exposed. At the same time, it has to be taken into account that Sr^{2+} amount in the coral skeletons depends on the environment in which different coral (sensus *genus*) live, as found already by Weber (1973).

Moreover, it was shown *in vitro* and *in vivo* (Marie, 2003; Marie, 2005,) that strontium bound to strontium ranelate reduces – inhibits – bone resoption, it increases bone formation and the mechanical properties of bones..

According to thermal reactivity factor – carbonate decay – the most reactive carbonate is in the sample V11, followed by the sample V12 which indicates their sedimental maturity and texture uniformity, which dictates the decarbonatisation conditions (Moropoulou et al, 2001). Similarly, reactive are also the coral and bryozoae, the samples V18 and V19. The carbonate content in the samples V9 and V10 coincide on one side with *Montastrea Cladocora* (from the western Australian reef) reactivity, on the other with the fossil species from *Calamophylliopsis flabellum* from the Jurrasic period (sample V14) and stromatophora *Ellipsactinia* (sample V15). Firstly, such reactivity of the carbonate component points to two geologically distinct environments of the material origins. Compared to the samples V1, V2 and V3, a totally different picture can be observed. This

indicates that the raw material source is unlikely to originate from geologically older or locally metamorphous regions. Nevertheless, the raw material could originate from fossil reef units that were spread over the entire European area in the Jurrasic period. (Turnšek, 1997).

Based on this data it can be concluded that carbonate extraction – for food products – is carried out in different ecological environment: (a) subaquatic, which is confirmed by samples V12 and V10, (b) possibly intertidal, which shows the sample V11, and (c) subaereal in the case of the sample V9. If the raw material originates from fossil corals or fossil mesosoic reefs, as indicated by the sample V12, it is the youngest one.

CONCLUSION

Based on the preliminary analyses we can conclude that regardless of the technological process used, the carbonate material differs in Sr^{2+} content according to its origin (rock or sediment). Sr^{2+} clearly indicates different diagenetic environments of origin of the raw material which in tern suggests the acquiring technology of it.

If the raw material originates from a dust-off or any other process that prevents emissions of the fine dust particles into environment, we cannot regard such a material as "waste material" in the sense of Oates (2003) since a raw material has a very high value on the market compared to extraction costs. Here an important question raises regarding firstly the environment preservation of very subtle subaquatic and intertidal ecosystems, and secondly the natural heritage, which indicate global fenomena.

ACKNOWLEDGEMENTS

The authors would like to thank Academic dr. Dragica Turnšek form SAZU-PIIR for corals determination.

LITERATURE

(1) AMIEL, A.J., FRIEDMAN, G.M. and MILLER, D.S. (1973) Distribution and nature of incorporation of trace elemnts in modern aragonitic corals. Sedimentology, 20, pp. 47–64.
(2) BARNES, R.D. and RUPPERT, E.E. (1993) Invertebrate Zoology. Brooks Cole. Rev Ed edition, 928 p.
(3) BUCCHI, R. (1980) Influence of the nature and preparation of raw materials on the reactivity of raw mix. In: 7th International Congress on the Chemistry of Cement, 1 Principal Reports. Paris. pp.1–43.
(4) BUCHARDT, B. and WEINER, S. (1981) Diagenesis of aragonite from Upper Cretaceous ammonites: a geochemical case-study. Seditnenfology, 28, pp. 423-438.
(5) COLMAN, T.B., HIGHLEY, D.E., GUNN, A.G., CAMERON, D.G. ans SMITH, B. (2003) *An assessment of the nature of the waste produced by active mineral workings in the UK*. Nottingham: British Geological Survey,

(6) DUNHAM, R. J. (1962) Classifications of Carbonate Rocks According To Depositional Texture. V Clasification of Carbonate Rocks, a Simposium. Ed.:Ham, E.W. Tulsa, pp. 108 –122.

(7) HOHENEGGER, J., YORDANOVA, E., NAKANO, Y. and TATZREITER, F. (1999) Habitats of larger foraminifera on the upper reef slope of Sesoko Island, Okinawa, Japan. Marine Micropaleontology, 36, pp. 109–168.

(8) JOHNSON, D. and CUFF, C. (1984) Holocene reef sequences and geochemistry, Britomart Reef, central Great Barier Reef, Australia. Sedimentology,31, pp 515–529.

(9) MOROPOULOU, A., BAKOLAS, A. and AGGELAKOPOULOU, (2001) E. The effects of limestone charateristics and calcination temperatuure to the reactivity of the quicklime. Cement and Concrete Research, 2001, 31, pp. 633-639.

(10) MACKENZIE, R.C. (1957) The differential thermal investigation of clays. London: Mineralogical society (clay minerals group), pp. 456.

(11) MARIE, J. P. (2003) Optimizing bone metabolism in osteoporosis: insight into the pharmacologic profile of strontium ranelate. Osteoporos. Int., 14, S9–S12.

(12) MARIE, J. P. (2005) Strontium ranelate: a novel mode of action optimizing bone formation and resorption. Osteoporos Int., S7–S10.

(13) OLSON, E. J., and CAZORT, R. J. (1969) Active calcium and strontium transport in human erythrocyte ghosts. J. Gen. Physiol. 53, pp. 311–322.

(14) PERRIN, C. (2004) Early diagenesis of carbonate biocrystals : isomineralogical changes in aragonite coral skeletons. Bulletin de la Société géologique de France,, 2, pp. 95–106.

(15) SINCLAR, D.J. and RISK, M.J. (2006) A numerical model of trace-element coprecipitation in a physicochemical calcification system: Application to coral biomineralization and trace-element 'vital effects'. Geochimica et Cosmochimica Acta, 70, pp. 3855–3868.

(16) SMITH, J.L. (2004) Bahamian stratigraphy: Estimating carbonate rock ages with mineralogy and diagenesis on San Salvador, Bahamas. Geological Society of America Abstracts with Programs,36, No.5, p. 68.

(17) TAYLOR, H.F.W. (1997) Cement Chemistry, 2nd ed. Oxford : Thomas Telford, pp. 439

(18) TURNŠEK, D. (1997) Mesozoic corals of Slovenia = Mezozojske korale Slovenije, Ljubljana : Znanstvenoraziskovalni center SAZU, Založba ZRC, pp. 512 .

(19) WEBER, J.N. (1973) Incorporation of strontium into reef coral skeletal carbonate. Geochimica et Cosmochimica Acta, 73, pp. 2173-2190

(20) WIGLEY, P. (1973) The distribution of strontium in limestone on Barbuda, West Indies. Sedimentology, 20, pp. 295-304.

(21) WOOD, S.A. and MAREK, C.R. (1993) "Recovery and Utilization of Quarry By-Products For Use in Highway Construction." *Proceedings of the Symposium on Recovery and Effective Reuse of Discarded Materials and By-Products for Construction of Highway Facilities,* Federal Highway Administration, Denver, Colorado, October.

(22) ZETHRAEUS, N., BORGSTRÖM, F., STRÖM, O., KANIS, J. A. and JÖNSSON, B. (2007) Cost-effectiveness of the treatment and prevention of osteoporosis – a review of the literature and a referene model. Osteoporosis Int., 8, 9–23.