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Alumino-Silicate Content in Calcium Supplements Derived from Various Carbonate Deposits

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Over the past 15 years, calcium (Ca) supplements have gained popularity as a means to supplement Ca deficient diets. Calcium carbonate ($CaCO_3$) is one of the most prevalent and least expensive forms of Ca used in the production of Ca supplements. This Ca salt was essentially synthesized by chemical precipitation, but now most manufacturers also offer products derived from ground oyster shells, often advertised as "natural source" Ca supplements. The $CaCO_3$ in the latter, however, does not originate from live or fresh shells, but actually consists of fossilized material quarried from geological deposits. In a previous study, Bourgoin and others (*in press*) noted that three brands of "shell-derived" Ca supplements contained two orders of magnitude more residue than that measured in mineral supplements composed of different Ca salts (i.e., Ca chelates and bonemeal). Detrital sediments, typically composed of alumino-silicate material, are often incorporated within carbonate deposits during sedimentation and early digenesis (Blatt *et al.* 1980) and may contribute to the residue content in Ca powders derived from fossilized shells. Consequently, this category of Ca supplement may contain important amounts of aluminum (Al); an element now accepted as one of the pathogenic factors in Alzheimer's disease (Crapper McLachlan 1991). Appreciable Al levels have previously been reported in mineral supplements made from dolomite ($CaMg(CO_3)_2$), another type of carbonate deposit (Roberts 1981, 1983).

This study measured the residue content in 19 brands of mineral supplements of which 9 brands were composed of dolomite and 10 brands were derived from fossilized oyster shells; referred to as "natural source" Ca supplements. The residues collected from 16 brands of the supplements were analyzed for their major constituents and were then compared to the chemical profiles listed for three marine sediment reference material (SRM) supplied by the National Research Council Canada. Aluminum concentrations were calculated and compared to previously reported Al levels in similar products.

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MATERIALS AND METHODS

Seven brands of "natural source" Ca supplements (F4 - F10) and 7 brands of dolomite-based products (D1 - D7) were purchased from various pharmacies and health food stores in Canada (Table 1). The US California Food and Drug branch supplied three additional brands of "natural source" Ca supplements (F1 - F3), as well as two brands made from dolomite (D8 - D9). The latter group was obtained directly at the processing plant and delivered to the lab as powders in plastic bags. Consequently, neither the mineral strength nor the suggested daily dosage could be reported for these two products (Table 1).

Table 1. Percent loss on ignition and residue content (dry weight) measured in 19 brands of mineral supplements. Mineral load was obtained from the product labels. "Dolomite" represents mineral supplements derived from dolomitic rock; "Fossil shells" represents "natural source " Ca supplements derived from fossilized oyster shells; ns: not specified.

Carbonate Matrix	Mineral Load		Loss on Ignition (%)	Residue Content (%)
	Ca	Mg		
	(mg/tablet)			
Dolomite				
D1	173	100	3.2%	0.9%
D2	140	75	3.0%	1.1%
D3	158	75	3.3%	1.7%
D4	158	75	2.9%	1.5%
D5	250	75	3.1%	1.4%
D6	200	ns	3.3%	1.5%
D7	250	ns	3.3%	1.1%
D8	ns	ns	0.7%	0.5%
D9	ns	ns	0.5%	0.6%
Fossil shells				
F1	500	ns	14.3%	9.4%
F2	500	ns	11.4%	6.4%
F3	250	ns	11.1%	4.9%
F4	500	ns	12.5%	6.2%
F5	500	ns	12.2%	6.8%
F6	650	ns	11.8%	7.4%
F7	500	ns	11.3%	7.6%
F8	500	ns	12.4%	8.9%
F9	500	ns	13.9%	9.5%
F10	650	ns	12.1%	9.7%

A total of 10 pills were weighed to estimate the mean tablet weight for each brand of mineral supplement. Previously weighed supplements were ashed (425°C) in a muffle furnace for 48 h, cooled in a desiccator and re-weighed to determine the loss on ignition (LOI). Sub-samples of the ashed powders were weighed (in triplicate), dissolved in 6 N HCl and filtered over pre-weighed Millipore membrane filters (0.45 μm). The residue-laden filters were dried (80°C) for 48 h, cooled in a desiccator and re-weighed to determine the residue content. The relative standard deviation associated to the residue content in any particular brand was never greater than 4 percent. Adequate amounts of ashed mineral supplements were dissolved and filtered to obtain approximately 1.5 g (dry weight) of residue. The residue samples were analyzed for their content of oxides of aluminum, silica, potassium and magnesium (Al_2O_3, SiO_2, K_2O and MgO; respectively) by X-ray fluorescence spectrometry (Phillips model PW 1450). The residues in three brands of mineral supplements (F2, D8, D9) could not be analyzed because of insufficient material.

RESULTS AND DISCUSSION

The Ca powders in the "natural source" Ca supplements contained approximately 6.5 times more residue than those of dolomite origin (Table 1). Although the sediment content in any type of carbonate deposit may vary considerably, dolomitic rock units often originate from evaporite sequences and contain relatively small amounts of clastic sediments. Conversely, limestones produced from massive shell beds (i.e., organic limestones) are often argillaceous because the cavities created by adjacent shell fragments (as well as the numerous borings within the shells) are later in-filled with fine grain sediments. It was not possible to identify the geological formations from which the mineral supplements were produced because the mining sites need not be disclosed to the general public. However, the XRF analyses indicated that the silica and aluminum oxides accounted for approximately 80 per cent of the residues obtained from the "natural source" Ca supplements (Fig. 1). The levels of these oxides and of the lesser abundant potassium and magnesium oxides, generally matched the levels of the same oxides listed for the marine SRMs (Fig. 1); suggesting that the bulk of the residues in the "natural source" Ca supplements were likely composed of detrital sediments. The oxide patterns associated with the residues of the dolomite mineral supplements did not readily match those listed for the marine SRMs (Fig 1). Considering that SiO_2 was added (listed ingredient) to most of the dolomite powders, it is unlikely that the bulk of the residues in these products originated from detrital sediments.

Most alumino-silicates in sediments are hydrated and will only release the bound water at moderately high temperatures (i.e., > 390°C). The higher sediment content in the "natural source" supplements could also explain why the LOIs within this category of supplements averaged about four times greater than those measured in the dolomite products (Table 1). Talc, a hydrated form of magnesium silicate ($Mg_3Si_4O_{10}(OH)_2$), was present (as an additive) in two brands of the "natural source" supplements (F1 & F9). Aside from accounting for the elevated MgO levels in these two products (Fig. 1), its presence may also explain why the LOIs measured in these two brands were significantly ($p < 0.05$) higher that those observed in other products within the same category of supplements (Table 1).

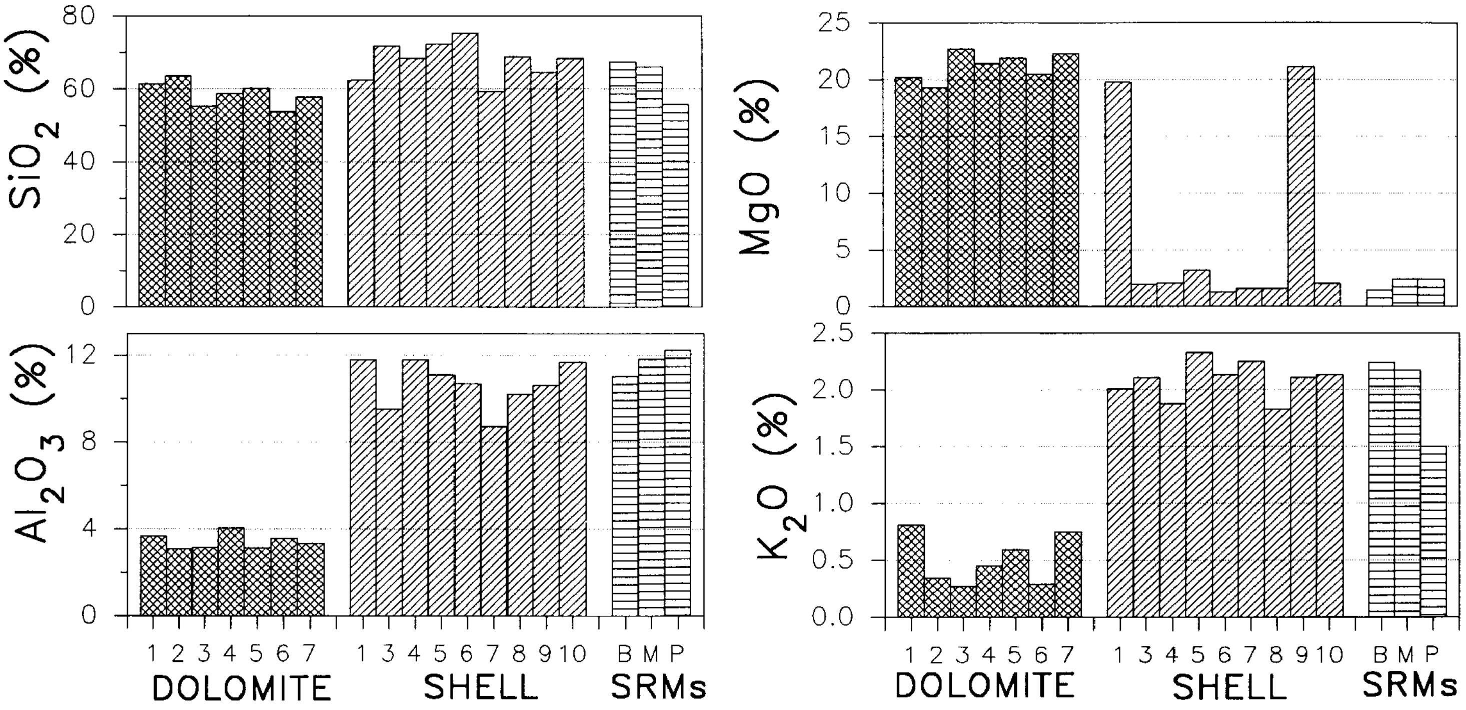

Figure 1 Oxide concentrations measured in 16 brands of mineral supplements and listed for three marine sediment reference materials (SRM). The numeric codes correspond to the mineral supplements listed in Table 1. The identifiers "B", "M" and "P" represent SRM codes BCSS-1, MESS-1 and PACS-1, respectively.

Aluminum concentrations, based on the Al_2O_3 content in the residues, were calculated for 16 brands of the mineral supplements (Table 2). All of the dolomite supplements analyzed in this study had Al levels comparable to that previously observed in similar products (Roberts 1983). The Al levels calculated for the nine brands of "natural source" Ca supplements were, however, substantially higher. In fact, they averaged an order of magnitude higher than Al levels reported in antacid tablets containing aluminum hydroxide as a major active ingredient (Table 2).

Table 2. Aluminum concentrations ($\mu g/g$) reported in various forms of mineral supplements and antacid tablets. The Al levels quoted for the products analyzed in this study were based on the Al_2O_3 content measured in the residues of the supplements.

Product Type	Al concentration ($\mu g/g$)	Brands Analyzed	References
dolomite	35 - 511	12	Roberts 1983
dolomite	171 - 315	7	this study
Ca carbonate	2421 - 5901	9	this study
antacid[1]	240 - 562	4	Schenk *et al.* 1991

[1] Aluminum hydroxide listed as a major active ingredient.

In the past 20 years, a considerable body of evidence has accumulated implicating Al in a variety of neurological dysfunctions. In Alzheimer's disease, for instance, intracellular sites of Al accumulation are nuclei of neurons, which bear neurofibrillary tangles, and senile plaques where alumino-silicates are found (Perl and Brody 1980; Candy *et al.* 1986). Although the gastrointestinal tract serves as an efficient barrier to absorption of Al, dietary sources are suspected. A recent study suggested that a public health effort to restrict human ingestion of Al may reduce the incidence of Alzheimer's disease in the elderly (Mclachlan *et al.* 1991). Aluminum is a ubiquitous element and normal adults consume approximately 3-5 mg of Al in the daily diet (Klein 1991). Based on a mean Al level calculated for the "natural source" Ca supplements (4370 μg Al/g), the ingestion of 2-3 tablets (suggested daily dosage listed on labels) of these products would supply approximately four to six times (12 mg Al) the average daily intake of Al. Comparatively, the amount of Al ingested from 3 dolomite-based supplements would only be a fraction of the normal dietary intake (ca. 0.4 mg Al). While it may be argued that the Al levels discussed in this study were based on a chemical form which may not be readily available to the human body (i.e., Al_2O_3), it should be stressed that the Al dissolved during the initial stage of the analysis was not measured and may be biologically, much more important. These arguments, however, are secondary to the main issue in that a significant amount of extraneous material which occurs in "natural source" Ca supplements is not listed on the product labels.

The current US federal regulation regarding labelling states that only incidental additives (i.e., substances used in processing or that migrate into the product from packaging or equipment) present at "insignificant" levels are exempt from the ingredients-labelling requirements (Kessler, 1989). It is interesting that while some labels of the "natural source" Ca supplements listed up to 17 ingredients (including titanium oxide), none of these included alumino-silicates which made up 10 percent (by weight) of some tablets. Furthermore, suggestive artwork, such as gaping oyster shells (sometimes containing a perl), depicted on some labels give the impression that these products are derived from fresh shells rather than quarried material. At least 25 percent of the women and 8 percent of children (2 to 6 y) in the US consume Ca supplements on a daily basis (Moss *et al.* 1989). These supplements are sold over the counter (i.e., non-prescription drugs) and the selection of a particular brand over another is usually based on the information provided on the label. Consequently, if "natural source" Ca supplements are to be made available to the general public, their content of relatively abundant and potentially harmful substances, such as alumino-silicates, should be clearly indicated on the labels.

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REFERENCES

Blatt H, Middleton G, Murray R (1980) Origin of sedimentary rocks (2nd edition) Prentice-Hall Inc., Englewood Cliffs, New Jersey

Bourgoin BP , Boomer D, Willie S, Edgar D, Evans D., Powell MJ Instrumental comparison for the determination of Cd and Pb in Ca supplements and other Ca-rich matrices. The Analyst (*in press*)

Candy, JM, Klinowski J, Perry RH, Perry EK, Fairbairn A, Oakley AE, Carpenter TA, Atack JR, Blessed G, Edwardson JA (1986) Aluminosilicates and senile plaque formation in Alzheimer's disease. The Lancet i:354-357

Crapper McLachlan DR (1991) Aluminum neurotoxicity: criteria for assigning a role in Alzheimer's disease. In: Lewis TE (ed) Environmental chemistry and toxicity of aluminum, Lewis Publishers Inc, Michigan, pp 299-315

Kessler DA (1989) The federal regulation of food labelling. N Engl J Med 321:717-725

Klein GL (1991) The aluminum content of parenteral solutions: current status. Nutr Rev 49:74-79

Mclachlan DRC, Kruck TP, Lukiw WJ, Krishnan SS (1991) Would decreased aluminum ingestion reduce the incidence of Alzheimer's disease. Can Med Ass J 145:793-804

Moss AJ, Levy AS, Kim I, Park YK (1989) Use of vitamin and mineral supplements in the United States: current users, types of products, and nutrients. Advance data from vital and health statistics; No. 174. Hyattsville, MD: National Center for Health Statistics

Perl DP, Brody AR (1980) Alzheimer's disease: X-ray spectrometric evidence of aluminum accumulation in neurofibrillary tangle-bearing neurons. Science 208:297-299

Roberts HJ (1981) Dolomite as a source of toxic metals. N Engl J Med 304:423

Roberts HJ (1983) Potential toxicity due to dolomite and bonemeal. So Med J 76:556-559

Schenk RU, Bjorksten J, Yeager L (1991) Composition and consequences of aluminum in water, beverages and other ingestibles. In: Lewis TE (ed) Environmental chemistry and toxicity of aluminum, Lewis Publishers Inc, Michigan, pp 247-269

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