

An experimental study of incongruent dissolution of CaCO_3 under analogue glacial conditions

Max R. McGILLEN,^{1,2} Ian J. FAIRCHILD^{1,3}

¹*School of Earth Sciences and Geography, Keele University, Keele, Staffordshire ST5 5BG, UK*

²*School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Sackville Building, Sackville Street, PO Box 88, Manchester M60 1QD, UK*

³*School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
E-mail: i.j.fairchild@bham.ac.uk*

ABSTRACT. This paper addresses the nature of incongruent dissolution of calcite in glacial settings using an experimental approach. Various CaCO_3 samples were comminuted using two contrasting techniques (dry machine-milling, and hand-grinding of an ice–water mixture) and dissolved to calcite saturation in both high- pCO_2 (10^{-2} atm) and low- pCO_2 ($10^{-3.5}$ = atmospheric) conditions. Ion yields of Ca, Mg and Sr were determined at the end of the experiments. Leachates displayed enhancement of Mg/Ca and Sr/Ca by a factor of 1.3–8.3 compared with bulk solid carbonate. Lower Mg/Ca and Sr/Ca ratios under higher- pCO_2 conditions reflect the percentage dissolution of the carbonate, not the pCO_2 per se. The experimental results imply that reported natural incongruent dissolution is readily reproducible in the laboratory and is primarily dependent on the water/rock ratio. Quantitative analysis of new and previous results suggests that the effect relates to the most reactive 0.15–0.25% of the sample, equating volumetrically to the outer few lattice layers, and it is interpreted as an anomalous leaching behaviour of calcite surfaces freshly exposed by crushing. This phenomenon could serve as an index of the relative efficiencies of fragmenting and dissolutional processes in glacial environments.

1. INTRODUCTION

Water–rock interaction is intensive in glacial environments, due to the high meltwater fluxes, the abundance of fresh surfaces, and the high specific surface area of subglacial sediments (e.g. Tranter and others, 1993, 1997; Fairchild and others, 1993, 1999a,b; Hubbard and Nienow, 1997; Mitchell and others, 2001; Brown, 2002). This interaction is intensified by the presence of reactive phases such as carbonates, which even in small quantities are influential upon meltwater chemistries (Fairchild and others, 1993; Tranter and others, 1993; Anderson and others, 1997; Blum and others, 1998; Skidmore and others, 2004). Previous experimental studies of carbonate and glacial till dissolution have dealt mainly with kinetic controls such as mixing processes and solution composition (e.g. Busenberg and Plummer, 1986; Velbel, 1993; Fairchild and others, 1994; Brown and others, 1996a,b, 2001), and there is a gap in the literature concerning the effects of particle attributes and pCO_2 upon the ion yields of glacial waters. Synthetic waters produced during experimentation are analogous to a variety of hydrological scenarios corresponding to different water/rock ratios. Particularly distinctive phenomena occur at low water/rock ratios, conditions analogous to those experienced by subglacial waters in prolonged contact with basal sediments (Brown, 2002). Here CaCO_3 saturation is approached or attained, comparable to ‘delayed flow’ waters described by Tranter and others (1993).

Where carbonate is abundant, anomalous dissolution behaviour has been observed, but it remains to be studied at lower carbonate contents. Fairchild and others (1994), working at Glacier de Tsanfleuron, Switzerland, found Mg/Ca and Sr/Ca ratios in meltwaters to be far higher than in the underlying bedrock. This enrichment of trace elements was duplicated by some simple laboratory experiments

performed on Tema-milled carbonates. Although this was initially attributed to the preferential dissolution of meta-stable marine relic carbonates (aragonite and Mg-calcite) hosted by the rock, Fairchild and Killawee (1995) demonstrated experimentally that these effects could occur in calcite lacking such relics. In other words, the CaCO_3 is releasing trace cations within its lattice preferentially with respect to Ca, a phenomenon referred to as incongruent dissolution. Fairchild and others (1999b) accepted incongruent calcite dissolution (together with aragonite dissolution locally) as the preferred interpretation of the Tsanfleuron data. Skidmore and others (2004) have also shown that there is a strong kinetic effect on $\delta^{13}\text{C}$ released during the early stages of carbonate dissolution (from both natural suspended sediment and reagent-grade powdered carbonate) that may represent a different expression of the same phenomenon. However, questions remain both as to whether the behaviour of the experimental materials is quantitatively representative of natural sediment, and as to the nature of the fundamental controls on this dissolution behaviour.

Typical comminution environments at the base of temperate glaciers consist of hydrous, low-temperature conditions. This contrasts with typical laboratory crushing methods (Tema-milling, ball-milling, etc.), which often generate high temperatures in anhydrous conditions. Energetic grinding conditions are known to affect particle attributes, some of which control reactivity and hence may influence dissolution congruence (e.g. ultrafine content (Ferret and others, 1987; Brown and others, 1996a; Anderson and others, 1997), surface energy (and therefore total free energy (Holdren and Speyer, 1985; Ferret and others, 1987) and crystal defect density (Holdren and Speyer, 1985; Ferret and others, 1987; Schott and others, 1989)). Overall, the expectation is that trace species should be preferentially released from a more damaged, intensely ground material.

Table 1. Experimental rock sample materials

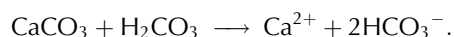
Sample	Age/location/lithology	Mineralogy	Insoluble residue %
D	Upper Cretaceous/UK/chalk (coccolith-rich micrite)	Calcite, quartz and phyllosilicates (illite)	9
E	Eocene/Tsanfleuron, Switzerland/organic-rich limestone	Calcite and phyllosilicates (illite and chlorite, originally clay)	9
H	Cretaceous (Hauterivian)/Tsanfleuron, Switzerland/limestone (echinoderm grainstone)	Calcite, quartz, feldspar, glauconite and other phyllosilicates (illite and chlorite, originally clay)	24
J	Carboniferous/Isle of Man, UK/single large calcite crystal (15 cm across)	Calcite	0.1
T	Cretaceous (Urgonian)/Tsanfleuron, Switzerland/limestone, grainstone	Calcite and quartz	4

Another important variable is pCO₂. At one extreme, in environments closed to resupply of CO₂, carbonate saturation is attained primarily by carbonate hydrolysis at pCO₂ values much lower than those of the atmosphere (Tranter and others, 1997). In meltstreams, carbonate dissolution can occur at close to atmospheric pCO₂ (10^{-3.5} atm), but organic acids and sulphuric acid derived from pyrite oxidation can lead to enhanced pCO₂ values (up to 10⁻² atm) similar to those developing in mature soils in proglacial environments (e.g. Fairchild and others, 1993, 1994; Tranter and others, 1993). It has also been posited that certain glacial environments earlier in Earth history existed under an atmosphere with enhanced pCO₂ (Hoffman and others, 1998).

At present there is no information on the role of solution pCO₂ as an independent variable. A possible role is implied by work on crushed materials which are reported to display anomalous (enhanced) dissolution kinetics (Ferret and others, 1987; Schott and others, 1989) since higher pCO₂ likewise enhances dissolution and so might promote incongruent dissolution. There are two potential roles for pCO₂: as a pH-related effect whereby higher-pCO₂ (and lower-pH) solutions tend to be more undersaturated and hence dissolve CaCO₃ more quickly, but also in terms of the total dissolved CO₂. These two effects are expressed, respectively, as the first and second terms of the classic dissolution equation of Plummer and others (1978):

$$R = k_1 \cdot (H^+) + k_2 \cdot a(H_2CO_3^*) + k_3 \cdot a(H_2O) - k_4 \cdot a(HCO_3^-),$$

where R is the reaction rate per unit area per unit time, k_1 – k_4 are rate constants, $a()$ are the activities of chemical species at the surface of the dissolving mineral, and $H_2CO_3^*$ refers to the sum of H_2CO_3 and dissolved CO₂. Both R and the rate constants have units of mass (dissolved) per unit surface area (of mineral) per unit time. The rate constant k_2 refers to the following reaction stimulated by aqueous CO₂:



The principal aim of this study is to constrain the controls on incongruent dissolution under a variety of analogous glacial conditions. Incongruent dissolution processes have been investigated using contrasting sample preparation methods and under different pCO₂ conditions. A synthesis of new and existing data leads to a new model for the phenomenon which could, in principle, be used to assess the balance of creation and destruction of new carbonate mineral surfaces in subglacial environments.

2. METHODS

In a previous study (Fairchild and others, 1994), milled limestone samples from the Tsanfleuron region were leached for comparison with glacial meltwaters. In the present study, representative examples of each of the three limestone types in the Tsanfleuron area were supplemented by two additional calcitic samples (Table 1). The additional samples were Cretaceous chalk and macrocrystalline calcite spar, whose expected response to grinding is disaggregation of primary particles and breakage of cleavage fragments respectively. For each powder, CaCO₃ is the only phase expected to show a measurable contribution to solutes by its dissolution, although samples E and H contain phyllosilicate minerals which could release some exchangeable ions.

One- to four-millimetre fractions of each material were obtained by coarse crushing; subsamples of these fractions were then either Tema-milled using an agate mill chamber for 90 s (for intensive grinding experiments), or ground for 60 s using an agate pestle and mortar in a deionized water-ice slurry (for gentle grinding experiments). These are referred to as milled and ice-crushed samples, respectively.

Dissolution of the powdered materials was carried out in open test tubes containing 10 mL of deionized water and 100 mg of the respective carbonate powder into which either laboratory air (pCO₂ = 10^{-3.5} atm) or 1% pCO₂ gas (pCO₂ = 10⁻² atm) was pumped. These are referred to as low-pCO₂ and high-pCO₂ conditions, respectively, in this study. A further set of experiments was carried out at high pCO₂ using around 300 mg of powder, in order to produce results with a similar percentage of dissolution to the low-pCO₂ experiments. Electroconductivity (EC) measurements were used to monitor reaction progress; typically samples required approximately 24 hours before dissolution ceased (no further rise in EC) and solutions could be considered to be in equilibrium. This inference was confirmed by pH and alkalinity measurements on some preliminary experiments in order to calculate calcite saturation index. Solutions were filtered through 0.45 µm papers and acidified with dilute Aristar-grade mineral acid prior to analysis by ion chromatography for Na, K, Mg and Ca (typical total precisions <5%) and graphite-furnace atomic absorption spectrophotometry for Sr (typically 10% precision). Aliquots (10 mg) of milled sample powder were dissolved in dilute solutions of Aristar-grade mineral acid, diluted, and analyzed as above to derive compositions of bulk carbonate. Insoluble residues were filtered and weighed. Samples viewed by scanning electron microscopy (SEM) were dried for 5 hours at 70°C (at higher temperatures annealing is possible) and gold-coated.

3. SEM OBSERVATIONS

Tema-milled samples had a more uniform grain-size (upper limit of around $30\ \mu\text{m}$) than samples of the same material crushed with ice using a pestle and mortar, but both preparation methods produced ultrafine particles (100–1000 nm; Fig. 1). Observed qualitatively, SEM images of milled samples display more ultrafine microparticles adhering to the surfaces of larger grains than ice-crushed samples (see Fig. 1a and b). However, this phenomenon may be an artefact of the preparation method, since a significant proportion of microparticles may have been dissolved in ice-crushed samples upon contact with water.

The sample of macrocrystalline calcite (sample J, Table 1) displays obvious cleavage surfaces (Fig. 1a and b). These would have facilitated development of microparticles. Even in this case, microparticles only cover a small proportion of the surface and will compose a subordinate part of the exposed surface area. Conversely, the chalk sample (sample D, Table 1) displayed very little generation of new microparticles, the dominant sub-micron-sized grains being separated coccolith platelets, typically 300–500 nm in size (Fig. 1c).

4. ION YIELDS AND DISSOLUTION BEHAVIOUR

Since the experiments were designed to approach calcite saturation fairly closely, their Ca contents should depend only on pCO_2 and not the water/rock ratio. Indeed, the experimental protocol yielded solutions with $24\text{--}29\ \text{mg L}^{-1}$ Ca under low- pCO_2 conditions and $73\text{--}82\ \text{mg L}^{-1}$ under high- pCO_2 conditions, consistent with calcite saturation in each case. For the experiments with 100 mg powder, the two different pCO_2 conditions led to different proportions of the rock powder being dissolved (0.65–0.86% of the total CaCO_3 in the samples at high pCO_2 and 1.8–2.7% at low pCO_2), allowing for varying insoluble residues, as in Table 1. Na and K data are not reported here, but it can be noted that Fairchild and Killawee (1995) found that a high proportion of bulk (dilute-acid soluble) Na and K was immediately released to solution from powdered carbonates, presumably from fluid inclusions or exchangeable sites on phyllosilicates.

Mg and Sr contents of the bulk sample powders are summarized in Table 2. If the carbonate dissolves congruently, Mg/Ca and Sr/Ca ratios should match those in the solid. Instead the ratios are systematically higher and so incongruent dissolution is occurring. The degree of incongruency can be expressed as the proportional increase in Mg/Ca or Sr/Ca relative to bulk carbonate (assuming Mg and Sr are entirely derived from carbonate). Values for this parameter for Mg/Ca range from 1.3 to 3.5 in the high- pCO_2 experiments and from 2.7 to 8.3 in the low- pCO_2 experiments, and values for Sr/Ca are comparable (Table 2).

Next we consider the effects of the two different grinding techniques on the degree of incongruency. Our expectation is that if there is a difference, milling should lead to stronger incongruent effects. However, Figure 2 illustrates that holding all other factors equal, samples differing only by the preparation method of the powder display relatively similar ion ratios (each enclosed by an ellipse in the figure). Figure 3 plots the enrichment or depletion percentage of the Mg/Ca and Sr/Ca ratios of the milled sample compared with the ice-crushed sample. The mean and standard deviation

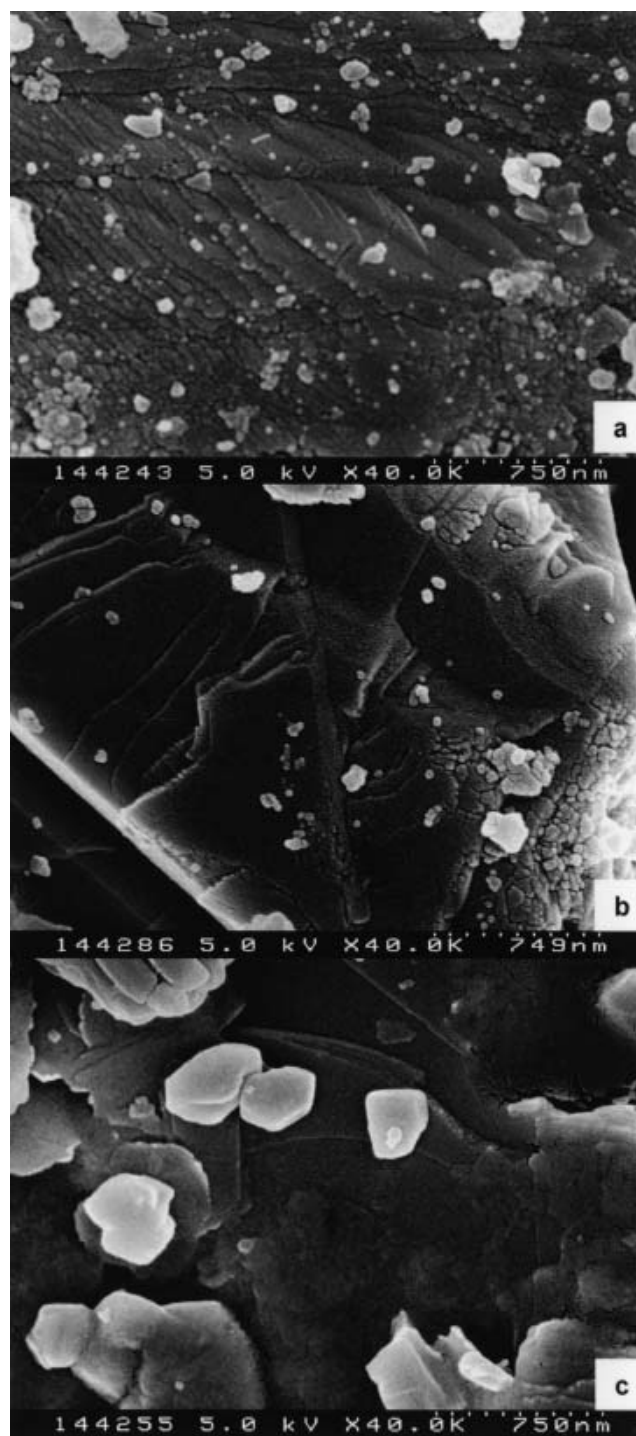


Fig. 1. High-magnification SEM images of experimental materials. (a) Milled sample J (macrocrystalline calcite) displaying cleavage surfaces and microparticles as small as 50 nm. (b) Ice-crushed sample J also displaying cleavage, but fewer microparticles. (c) Milled sample D (chalk) with well-formed sub-micron-sized crystals representing fragments of coccolith fossils.

for the Mg/Ca enrichment is $6 \pm 12\%$ and for Sr/Ca is $7 \pm 18\%$, i.e. within error of zero. The largest enrichment of the milled powder (34%) was found for Mg/Ca ratios in sample T in low- pCO_2 experiments. A further three replicates involving each of the two powder preparation methods were made and the mean Mg/Ca of the total four milled samples was now found to be slightly less than that of the ice-crushed samples, at 0.019 ± 0.02 compared with

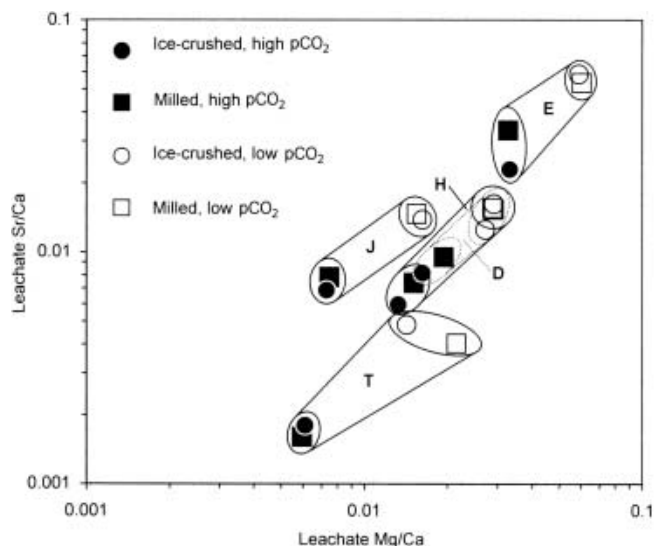


Fig. 2. Cross-plot of leachate Sr/Ca vs Mg/Ca (mass ratios) from a suite of experiments for ice-crushed and milled powders under high- and atmospheric- $p\text{CO}_2$ conditions. Ice-crushing and milling using 100 mg powder per 100 mL solution. Experiments on the same powder at the same $p\text{CO}_2$ are enclosed within a small ellipse to emphasize their similarity compared with the different results obtained at differing $p\text{CO}_2$, attributed to the differing dissolution percentages of the sample.

0.021 ± 0.12 . The high standard deviation of the ice-crushed samples indicates sample heterogeneity which could explain the initial result. In summary, there is no statistical difference between Mg/Ca and Sr/Ca yields of milled and ice-crushed samples within a 12–18% experimental variability which is probably caused by sample heterogeneity.

In contrast to the similarity of samples differing only in powder preparation technique, there is a clear separation of the samples leached under high- $p\text{CO}_2$ conditions and those under low- $p\text{CO}_2$ conditions (Fig. 2). However, this does not demonstrate that $p\text{CO}_2$ is the direct control since Fairchild and others (1994) showed that the Mg/Ca and Sr/Ca ratios were a strong function of percentage of dissolution of the sample carbonate (this parameter was adjusted using different water/rock ratios) and this is true also for the new data in Table 2. If the elevated Mg/Ca and Sr/Ca ratios observed in low- $p\text{CO}_2$ experiments were a direct function of $p\text{CO}_2$, they should be independent of the proportion of the sample

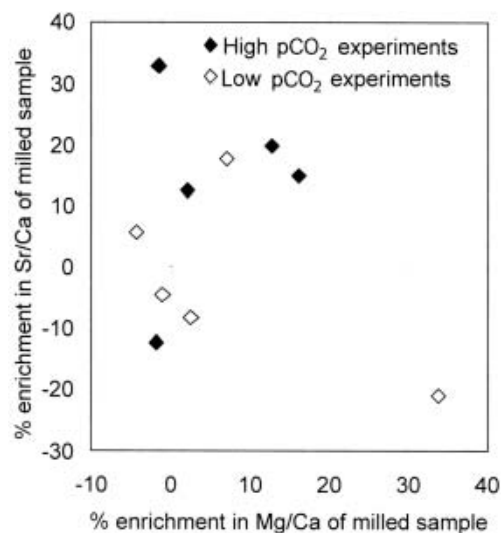


Fig. 3. Comparison of the Mg/Ca and Sr/Ca ratios of milled samples with those of ice-crushed samples expressed as a percentage of enrichment of milled samples. In both high- and low- $p\text{CO}_2$ experiments both enrichment and depletion in Mg/Ca and Sr/Ca occurs in milled samples. The method of powder preparation evidently does not have a strong effect on leachate properties.

dissolved. Testing this assertion is the purpose of the additional set of high- $p\text{CO}_2$ samples in which close to 300 mg of sample powder was used per 100 mL solution in order to produce lower percentage dissolutions (lower water/rock ratio), similar to those of the original low- $p\text{CO}_2$ experiments. Figure 4 shows that for each powder these additional high- $p\text{CO}_2$ experiments successfully matched both the 0.5–1% dissolution and the enhanced Mg/Ca of the low- $p\text{CO}_2$ experiments. Percentage carbonate dissolution, not $p\text{CO}_2$, is thus the main control.

5. DISCUSSION

In previous work, there have been conflicting claims as to whether dry laboratory grinding can be regarded as analogous to natural comminution processes (e.g. Dandurand and others, 1982), or whether, in a glacial context, the analogy should only be applied to the comminution environments of 'dry' (cold)-based glaciers (Petrovich, 1981). Although it is now recognized that an interfacial water film is present in cold-based glaciers (e.g. Cuffey and others, 1999), this film

Table 2. Dissolution behaviour of trace ions

Sample	Concentration in CaCO ₃		Proportional increase in Mg/Ca or Sr/Ca relative to bulk CaCO ₃ in experiments with 100 mg powder/100 mL solution			
	Mg mg kg ⁻¹	Sr mg kg ⁻¹	High (10 ⁻²) pCO ₂ experiments		Low (10 ^{-3.5}) pCO ₂ experiments	
			Mg	Sr	Mg	Sr
D	2030	990	3.5	3.5	5.6	5.5
E	8750	6170	1.5	1.8	2.8	3.6
H	4330	1730	1.3	1.5	2.7	3.6
J	1490	1930	2.0	1.5	4.3	2.9
T	940	280	2.6	2.4	8.3	6.4

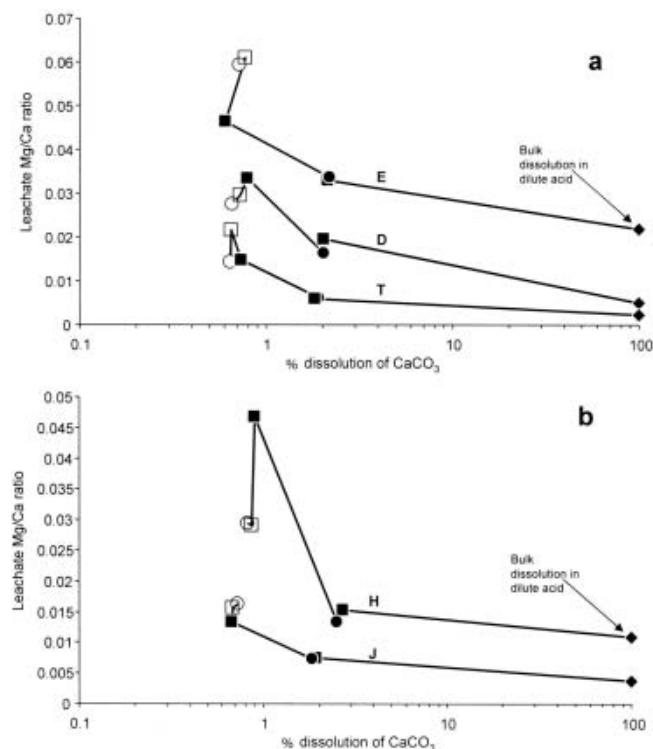


Fig. 4. Leachate Mg/Ca (mass ratio) plotted against the percentage of CaCO₃ in the sample powder calculated to have dissolved during the dissolution experiment for (a) powders E, T and D and (b) powders H and J. Symbols as for Figure 2. Results for high-pCO₂ experiments differ according to the water/rock ratio; the 300 mg per 100 mL experiments (at 0.5–1% dissolution) have similar Mg/Ca ratios to 100 mg per 100 mL experiments run at low pCO₂.

would have a high solute content that would limit water/rock interaction.

Fairchild and others (1994) found that partial dissolution of dry-milled limestones yielded similar incongruent dissolution effects to the Tsanfleuron catchment, but we have now demonstrated directly, within the 10–20% uncertainty of sample heterogeneity, that wet sample preparation (hand-crushing in an ice–water slurry) yields results comparable with those of brief sample dry milling. Caution does need to be expressed, however, about the nature of the dry grinding. The dry grinding period in our study was short. Under longer grinding, energy is stored internally, for example by creation of crystal dislocations (Dandurand and others, 1982), and different kinds of behaviour might be observed.

The experiments performed under different pCO₂ conditions show that, provided the water/rock ratio is held constant, pCO₂ has no effect on the degree of incongruity during weathering. Since pCO₂ influences the rate of dissolution, this implies that the incongruity is not primarily a function of enhanced dissolution kinetics related to sample crushing and creation of internal damage. Conversely, the proportion of the powder dissolved (determined by a combination of water/rock ratio and pCO₂) is confirmed as being the main variable influencing ion ratios. Previously it was noted that low-water/rock-ratio weathering environments, such as till and sediment-rich basal ice, yielded waters with high Mg/Ca and Sr/Ca ratios because of incongruent dissolution effects (Fairchild and others, 1999b). In contrast, low ion ratios result from dissolution in

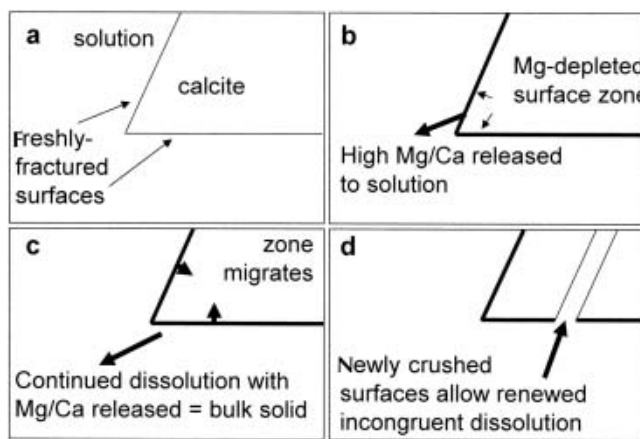


Fig. 5. Conceptual model to account for the occurrence of the incongruent dissolution phenomena involving the creation of Mg-depleted surface layers given sufficient leaching following crushing of calcite.

high-water/rock-ratio environments such as suspended sediment in meltstreams (Fairchild and others, 1999a).

6. A MODEL FOR INCONGRUENT DISSOLUTION AT FRESHLY CREATED CALCITE SURFACES

Two types of model can be envisaged for the dissolution behaviour. One is a wholly dissolutional model, whereby ions are detached from the crystal and the incongruent dissolution behaviour reflects enhanced loss of trace elements to solution at energetically favourable sites. The second is a dissolution–reprecipitation model (Ostwald’s ripening; Fairchild and others, 1994) whereby the most soluble materials dissolve and reprecipitation occurs on other surfaces. The partitioning behaviour of calcite tends to exclude Mg and Sr and so they would preferentially remain in solution. Some observations militate against the second type of model. Firstly, the incongruent reaction occurs very rapidly, whereas ripening of calcite tends to occur over a longer period (Dandurand and others, 1982). Secondly, ripening of wet-crushed materials would be dependent on the occurrence of microparticles with enhanced surface energy. However, the abundance of microparticles is variable, as discussed earlier, and does not appear to relate to the consistent occurrence of incongruent behaviour. Accordingly we prefer a wholly dissolutional model.

Conceptually and geometrically the simplest form of the model is that the incongruent dissolution reflects a behaviour of newly created surfaces as they adjust to the surrounding solution (Fig. 5). Preferential leaching of Mg over Ca relative to the bulk Mg and Ca compositions is posited to occur in an outer layer (Fig. 5b) and this is the attributed cause of the incongruent dissolution. One can then envisage the establishment of a steady-state condition such that the Mg-depleted layer migrates as the crystal dissolves and ratios of ions released to the solution are the same as the bulk crystal composition (Fig. 5c). Renewed crushing starts the cycle anew (Fig. 5d). Somewhat similar behaviour has already been shown to operate in the case of the carbonate mineral dolomite ((CaMg(CO₃)₂) by Busenberg and Plummer (1982). These authors found that preferential leaching of Ca from the outer lattice layer of fresh surfaces occurred, but that subsequent dissolution was

congruent. Whereas in calcite, Mg is a 'foreign' ion in Ca sites, excess Ca in Mg sites commonly occurs in dolomite.

A possible way of conceiving why the leached layer should occur in calcite is in terms of the equilibrium Mg/Ca ratios of solid and solution in contact. This is defined in terms of a partition coefficient (K) where

$$\text{Tr}/\text{Ca}_{\text{CaCO}_3} = K \cdot \text{Tr}/\text{Ca}_{\text{solution}}$$

Here, Tr is the trace element or species and Ca is the major species calcium. Values of K for Mg and Sr in calcite are much less than 1 (Morse and Bender, 1990). Congruent dissolution results in ion ratios identical to those of the dissolving phase, whereas the Mg/Ca and Sr/Ca ratios of a solid in equilibrium with a solution will be much lower than that in the solution. Accordingly, there will arguably be a tendency to lose additional Mg and Sr to the solution. More generally, the model is consistent with observations of high mobility of other ions close to the calcite surface (Stipp and others, 1998) leading to the concept of this region as a dynamic zone in which elements may be either enriched or depleted with respect to the bulk lattice (Watson, 2004).

The dissolution model is now presented in quantitative terms and its assumptions tested, based both on the new data and on data previously presented by Fairchild and others (1994). We apply the model to Mg data, but Sr could be treated in an analogous way. In order to set up the model, two assumptions need to be made. The first is that the dissolving species represent a mixture of two components of constant composition, one corresponding to the bulk powder composition, and a second component enriched in Mg, reflecting the 'pure' incongruent behaviour (i.e. the transformation of the outer part of the crystal into the Mg-depleted layer). When calcite dissolves completely, the second component does not manifest itself, whereas when only partial dissolution occurs the congruent dissolution is supplemented by the second component. The second assumption is that the crystal surface develops the Mg-depleted surface layer as the first response when it comes in contact with solution following the creation of the new surface. The development of this layer is associated with the release of Mg and Ca to solution with a characteristically high Mg/Ca ratio. The Mg-depleted layer is only incompletely developed if the total percentage of carbonate dissolution is less than that required to develop the layer.

The mass balance is expressed as follows:

$$\text{Mg}_1 + \text{Mg}_2 = \text{Mg}_{\text{tot}}, \quad (1)$$

where 1 refers to Mg derived from bulk dissolution, 2 refers to Mg derived from the 'pure' incongruent dissolution component and tot refers to the total Mg in solution. Likewise for Ca:

$$\text{Ca}_1 + \text{Ca}_2 = \text{Ca}_{\text{tot}}. \quad (2)$$

The bulk composition (ratio R_1) can be found by total acid dissolution of the powder:

$$R_1 = \text{Mg}_1/\text{Ca}_1. \quad (3)$$

Likewise the (unknown) ratio of the 'pure' incongruent behaviour (R_2) is defined as:

$$R_2 = \text{Mg}_2/\text{Ca}_2. \quad (4)$$

These equations can be solved by positing values for R_2 and then testing the consistency of results from different experiments. If there is sufficient dissolution to cause complete development of the Mg-depleted surface layers,

both Mg₂ and Ca₂ will reach a constant value for a powder of given surface area. Ca₂ is re-expressed as a percentage of dissolution by defining a parameter F (the percentage of the Ca in the solid powder dissolved from 'pure' incongruent sites, i.e. that leached during the formation of the outer Mg-depleted layer, during the experiment), defined as:

$$F (\%) = (\text{Ca}_2 \cdot V/1000)/(0.4M) \cdot 100, \quad (5)$$

where Ca₂ has units of mg L⁻¹, V is the solution volume in millilitres, 0.4 refers to the mass fraction of Ca in CaCO₃ and M is the mass of the powder in milligrams. This parameter is analogous to, but differs from, percentage of dissolution, as used in Figure 3, which represents the percentage of total powder dissolved:

$$\% \text{ dissolution} = (\text{Ca}_{\text{tot}} \cdot V/1000)/(0.4M) \cdot 100. \quad (6)$$

Values of F for different experiments should be constant, according to the second assumption above, except at the lowest possible dissolution.

The value of R_2 must be at least as large as the largest value of Mg_{tot}/Ca_{tot} found in the experiments. The highest values were found in the work of Fairchild and others (1994), who extended dissolution to low water/rock ratios in water-powder slurries with dissolution values as low as 0.03–0.06%. The degree of incongruity inferred from the solute yields was found to be three or four times higher than that observed at about 1% dissolution. If one chooses a value of R_2 just above the maximum values obtained of Mg_{tot}/Ca_{tot} at 0.03–0.06% dissolution, the values of F obtained are internally consistent as is now explained. The values of F at 0.5–10% dissolution, calculated from the data in Fairchild and others (1994), are around 0.15%, but drop to values below 0.1% when the total dissolution is itself less than 0.1% of the total carbonate powder. This conforms to the second assumption used to set up the model as above. However, if higher values of R_2 are used, all values of F drop proportionally and hence the model violates the second assumption.

In applying the same approach to the new experimental data (Figs 2 and 3), values for R_2 are assigned to be about three times higher than those observed at around 1% dissolution. When this is done, consistent values of F are obtained with average values of 0.15–0.24% for the five samples investigated. In conclusion, all the experimental results are consistent with a model in which a surface Mg-depleted layer is preferentially developed when freshly created calcite surfaces are exposed to aqueous fluid. The surface layers require about 0.5% of the total carbonate to dissolve to develop completely, and themselves make up around 0.2% of the bulk sample.

Assuming cubic geometry, 0.2% of the sample corresponds to a surface layer whose thickness is 1/3000 of the mean diameter of the particles. Given a mean particle size of a few microns, the thickness of this surface layer would be on a nanometre scale. Hence, the phenomenon of 'pure' incongruent dissolution, corresponding to the development of the Mg-depleted surface layer, would correspond to the dissolution of a thickness of one or two unit cells to yield the required Ca and 10–30 unit cells for Mg (or less if Mg were concentrated at defect sites). The model is thus internally consistent, but further experimental work utilizing repeat leaching with and without further crushing would be desirable to test its assumptions further.

There are parallels with the recent work on anomalously light $\delta^{13}\text{C}$ signatures of carbon released during the experimental analogue glacial dissolution of carbonates by Skidmore and others (2004). These authors favoured a kinetic isotope fractionation model involving preferential dissolution of ultrafine particles, although they made no direct observations of particle attributes. The model offered herein also appears consistent with their data. Integration of isotopic and elemental approaches in future work should prove fruitful.

7. IMPLICATIONS FOR STUDY OF GLACIAL PROCESSES

There is currently interest in developing criteria for understanding the degree of comminution of material in different glacial environments (Scherer and others, 2004), and a reassertion of the potential importance of supraglacial environments in the physical breakdown of rock material (Owen and others, 2003). The work presented here suggests a novel approach to evaluating the extent to which unweathered calcite surfaces are present, and hence to judging the balance of creation of such surfaces by physical forces, and their destruction by dissolution. There might be implications for reconstruction of thermal regimes since dissolution would be minimized under cold-based glaciers.

A corollary of the incongruent dissolution model is that the phenomenon should disappear when dissolution of a significant (>0.5%) proportion of the carbonate occurs in the case of a till with the same specific surface area as the powders used in the experiments. In such sediments composed entirely of calcite, substantial water movement through till or basal ice would be needed to dissolve this much sediment. (In pore-water filling of a carbonate till with 50% porosity, only 0.002% of the till carbonate need be dissolved to attain calcite saturation.) The incongruent phenomenon would be significantly more persistent if the mean grain-size were much less than the typical milled sizes of 20–30 μm since specific surface area is directly proportional to the reciprocal of grain diameter. Dreimanis and Wagners (1969) proposed a terminal grade for carbonates of around 2 μm , although such a grade would take a long transport path to develop. Evidence from Glacier de Tsanfleuron (Fairchild and others, 1999b), where incongruent dissolution effects are strong in meltwater chemistry, indicates that in an active subglacial environment rich in carbonate, creation of new surfaces by crushing and grinding of carbonate sediment is likely to strongly outpace dissolution processes.

However, an intriguing possibility is that in carbonate-poor glacial sediments dissolution processes may be close to keeping pace with physical processes. For example, at Haut Glacier d'Arolla, Switzerland, carbonate contents of sediments are of the order of 1% (Brown and others, 1996b; Fairchild and others, 1999a), but contribute much more strongly to solute fluxes. Here incongruent dissolution of carbonate could be restricted to regions which experience recent high rates of crushing. In other words, the presence or absence of incongruent dissolution effects could serve as an index of the recent balance of physical deformation and water movement through a subglacial environment. Sophisticated techniques are now available to distinguish carbonate and silicate sources (e.g. Bickle and others, 2005) and so a distinctive carbonate contribution to solutes can be specified even in silicate-dominated bedrocks.

ACKNOWLEDGEMENTS

The experiments were enabled by a 2002 bursary from the Nuffield Foundation. We thank I. Wilshaw for technical assistance, and B. Hubbard and an anonymous reviewer for incisive comments that led to significant improvements in the manuscript under the guidance of editor J. Hart.

REFERENCES

- Anderson, S.P., J.I. Drever and N.F. Humphrey. 1997. Chemical weathering in glacial environments. *Geology (Boulder)*, **25**(5), 399–402.
- Bickle, M.J. and 6 others. 2005. The relative contributions of silicate and carbonate rocks to riverine Sr fluxes in the headwaters of the Ganges. *Geochim. Cosmochim. Acta*, **69**(9), 2221–2240.
- Blum, J.D., C.A. Gazis, A.D. Jacobson and C.P. Chamberlain. 1998. Carbonate versus silicate weathering in the Raikhot watershed within the High Himalayan Crystalline Series. *Geology (Boulder)*, **26**(5), 411–414.
- Brown, G.H. 2002. Glacier meltwater hydrochemistry. *Appl. Geochem.*, **17**(7), 855–883.
- Brown, G.H., M. Tranter and M.J. Sharp. 1996a. Experimental investigations of the weathering of suspended sediment by Alpine glacial meltwaters. *Hydrol. Process.*, **10**, 579–598.
- Brown, G.H., M. Sharp and M. Tranter. 1996b. Subglacial chemical erosion: seasonal variations in solute provenance, Haut Glacier d'Arolla, Valais, Switzerland. *Ann. Glaciol.*, **22**, 25–31.
- Brown, G.H., B. Hubbard and A.G. Seagren. 2001. Kinetics of solute acquisition from the dissolution of suspended sediment in subglacial channels. *Hydrol. Process.*, **15**, 3487–3497.
- Busenberg, E. and L.N. Plummer. 1982. The kinetics of dissolution of dolomite in CO₂–H₂O systems at 1.5 to 65°C and 0 to 1 atm PCO₂. *Am. J. Sci.*, **282**, 45–78.
- Busenberg, E. and L.N. Plummer. 1986. A comparative study of the dissolution and crystal growth kinetics of calcite and aragonite. *US Geol. Surv. Bull.* 1578, 139–168.
- Cuffey, K.M., H. Conway, B. Hallet, A.M. Gades and C.F. Raymond. 1999. Interfacial water in polar glaciers and glacier sliding at –17°C. *Geophys. Res. Lett.*, **26**(6), 751–754.
- Dandurand, J., R. Gout and J. Schott. 1982. Experiments on phase transformations and chemical reactions of mechanically activated minerals by grinding: petrogenetic implications. *Tectonophysics*, **83**, 365–356.
- Dreimanis, A. and U.J. Wagners. 1969. Lithologic relation of till to bedrock. In Wright, H.E., ed. *Quaternary geology and climate*. Ottawa, Royal Society of Canada, 11–49.
- Fairchild, I.J. and J.A. Killawee. 1995. Selective leaching in glacierized terrains and implications for retention of primary chemical signals in carbonate rocks. In Kharaka, Y. and O.V. Chudaev, eds. *Proceedings of the 8th International Symposium on Water/Rock Interactions, Vladivostok, Russia*. Rotterdam, A.A. Balkema, 79–82.
- Fairchild, I.J., L. Bradby and B. Spiro. 1993. Reactive carbonate in glacial systems: a preliminary synthesis of its creation, dissolution and reincarnation. In Deynoux, M., J.M.G. Miller, E.W. Domack, N. Eyles, I.J. Fairchild and G.M. Young, eds. *Earth's glacial record – ICGP Project 260*. Cambridge, etc., Cambridge University Press, 176–192.
- Fairchild, I.J., L. Bradby, M. Sharp and J.L. Tison. 1994. Hydrochemistry of carbonate terrains in alpine glacial settings. *Earth Surf. Process. Landf.*, **19**(1), 33–54.
- Fairchild, I.J., J.A. Killawee, B. Hubbard and W. Dreybrodt. 1999a. Interactions of calcareous suspended sediment with glacial meltwater: a field test of dissolution behaviour. *Chem. Geol.*, **155**(3–4), 243–263.
- Fairchild, I.J. and 6 others. 1999b. Solute generation and transfer from a chemically reactive alpine glacial–proglacial system. *Earth Surf. Process. Landf.*, **24**(13), 1189–1211.

- Ferret, J., Y. Gout, Y. Kihn and J. Sevely. 1987. The influence of grinding on the dissolution kinetics of calcite. *Phys. Chem. Miner.*, **15**, 163–170.
- Hoffman, P.F., A.J. Kaufman, G.P. Halverson and D.P. Schrag. 1998. A Neoproterozoic snowball Earth. *Science*, **281**(5381), 1342–1346.
- Holdren, G.R. and P.M. Speyer. 1985. Reaction rate–surface area relationships during the early stages of weathering. I. Initial observations. *Geochim. Cosmochim. Acta*, **49**(3), 675–681.
- Hubbard, B. and P. Nienow. 1997. Alpine subglacial hydrology. *Quat. Sci. Rev.*, **16**(9), 939–955.
- Mitchell, A., G.H. Brown and R. Fuge. 2001. Minor and trace element export from glacierized Alpine headwater catchment (Haut Glacier d’Arolla, Switzerland). *Hydrol. Process.*, **15**(18), 3499–3524.
- Morse, J.W. and M.L. Bender. 1990. Partition coefficients in calcite: examination of factors influencing the validity of experimental results and their application to natural systems. *Chemical Geol.*, **82**, 265–277.
- Owen, L.A., E. Derbyshire and C.H. Scott. 2003. Contemporary sediment production and transfer in high-altitude glaciers. *Sediment. Geol.*, **155**(1–2), 13–36.
- Petrovich, R. 1981. Kinetics of dissolution of mechanically comminuted rock-forming oxides and silicates – II. Deformation and dissolution of oxides and silicates in the laboratory and at the Earth’s surface. *Geochim. Cosmochim. Acta*, **45**(10), 1675–1686.
- Plummer, L.N., T.M.L. Wigley and D.L. Parkhurst. 1978. The kinetics of calcite dissolution in CO₂ water systems at 5° to 60°C and 0.0 to 1.0 atm CO₂. *Am. J. Sci.*, **278**, 179–216.
- Scherer, R.P., C.M. Sjunneskog, N.R. Iverson and T.S. Hooyer. 2004. Assessing subglacial processes from diatom fragmentation patterns. *Geology*, **32**(7), 557–560.
- Schott, J., S. Brantley, D. Crerar, C. Guy, M. Borcsik and C. Wil-laime. 1989. Dissolution kinetics of strained calcite. *Geochim. Cosmochim. Acta*. **53**(2), 373–382.
- Skidmore, M., M. Sharp and M. Tranter. 2004. Kinetic isotopic fractionation during carbonate dissolution in laboratory experiments: implications for detection of microbial CO₂ signatures using d¹³C-DIC. *Geochim. Cosmochim. Acta*, **68**(21), 4309–4317.
- Stipp, S.L., J. Konnerup-Madsen, K. Franzreb, A. Kulik and H.J. Mathieu. 1998. Spontaneous movement of ions through calcite at standard temperature and pressure. *Nature*, **396**(6709), 356–359.
- Tranter, M., G. Brown, R. Raiswell, M. Sharp and A. Gurnell. 1993. A conceptual model of solute acquisition by Alpine glacial meltwaters. *J. Glaciol.*, **39**(133), 573–581.
- Tranter, M. and 9 others. 1997. Variability in the chemical composition of *in situ* subglacial meltwaters. *Hydrol. Process.*, **11**(1), 59–78.
- Velbel, M.A. 1993. Constancy of silicate-mineral weathering-rate ratios between natural and experimental weathering: implications for hydrologic control of differences in absolute rates. *Chem. Geol.*, **105**, 89–99.
- Watson, E.B. 2004. A conceptual model for near-surface kinetic controls on the trace-element and stable isotope composition of abiogenic calcite crystals. *Geochim. Cosmochim. Acta*, **68**(7), 1473–1488.

MS received 14 August 2004 and accepted in revised form 14 July 2005