INTRODUCTION
Calcite (CaCO₃), is the most common of all the carbonate minerals, and has been comprehensively studied from both an experimental and theoretical viewpoint. Its surface reactivity is a key factor in the chemical control of aquatic environments, in diagenesis, in the cycling and entrapment of metal contaminants, the biogeochemical cycle of carbon, and in a variety of industrial processes (e.g., Morse and Arvidson 2002). Calcite is also important in controlling many biomineralization processes, and it has recently been shown to exhibit chiral morphologies in the presence of amino acids (Orme et al. 2001). In order to understand the factors that control calcite growth, dissolution, and reactivity, we must first have an accurate description of the atomic-scale structure of the surface itself. The (101–4) cleavage surface of calcite has been extensively studied using low energy electron diffraction (LEED) (Stipp and Hochella 1991), atomic force microscopy (AFM) (Ohnesorge and Binning 1993), X-ray photoelectron spectroscopy (XPS) (Stipp and Hochella 1991), and X-ray reflectivity (Fenter et al. 2000). Stipp and Hochella (1991) showed that calcite cleaved in vacuum gave a LEED pattern with weak spots indicative of a (2 × 1) surface supercell. Such a supercell was also observed when samples were cleaved in air and covered with a monolayer of water (Stipp et al. 1994). Other studies of wet calcite surfaces using AFM (Ohnesorge and Binning 1993; Liang et al. 1996; Rachlin et al. 1992) and X-ray reflectivity (Fenter et al. 2000) have all reported a (1 × 1) symmetry for the (1014) surface.

One might expect that molecular modeling would have been utilized to resolve this issue, given its past success in modeling surfaces where experimental data can sometimes lag behind the computed predictions. For example, the basal plane of alumina was predicted to undergo extensive surface relaxation in 1987 (Mackrodt et al. 1987), which was only experimentally verified recently. However, atomistic calculations (de Leeuw and Parker 1997; Wright et al. 2001) of wet and dry (1014) calcite surfaces have failed to report evidence for a (2 × 1) reconstruction. One possible reason for this is that interatomic potentials fitted to bulk properties are not guaranteed to be valid for lower coordination environments, such as those found at surfaces.

In order to resolve the debate concerning the nature of the termination of the dominant face of calcite, and to demonstrate that molecular modeling of complex surfaces using interatomic potentials can be a key tool in surface analysis, we have developed a new, more accurate, calcite potential model. In particular, we have included information on the structure and energetics of molecular calcium carbonate species in the derivation in order to ensure that low coordination environments are properly described, as well as the features of bulk materials. This work has been performed in tandem with extending the GULP bulk simulation code (Gale 1997), with its myriad of facilities, to surfaces.

THEORETICAL PROCEDURE
There have been numerous attempts to derive a satisfactory force field for the description of the polymorphs of calcium carbonate (Dove et al. 1992a; Pavese et al. 1996). Of these, arguably the most accurate in terms of the description of the structure and physical properties of both calcite and aragonite...