Growth and dissolution characteristics of dolomite studied in ultrathin section: a new TEM approach

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Introduction

A sample preparation technique involving ultramicrotomy is presented for the preparation of ultrathin sections of single crystals of synthetic calcite and natural dolomite cements. This technique offers certain advantages over the conventional ion-thinning technique (Wenk *et al.*, 1983) since more material can be prepared and surveyed more quickly by transmission electron microscopy (TEM). On the other hand, the high shear strain involved in ultramicrotomy induces a nearly pervasive microcleavage parallel to $\{10\bar{1}4\}$ and only fragments from the original crystal are recovered. However, individual crystal fragments remain largely coherent and the nearly-pervasive microcleavage highlights differences in the physical properties among different carbonate phases. TEM observations of ultrathin sections from diagenetic dolomites show that the microcleavage is not necessarily uniform through single growth sectors and reveal a pronounced domain structure. The effect of intracrystalline compositional and structural heterogeneity on the reactivity of carbonate minerals can also studied qualitatively by exposing ultrathin sections to various solutions directly on a TEM grid.

Samples and methods

The dolomite crystals selected for this study are from subsurface cores collected from the Upper Devonian dolomitized buildups along the Rimbey-Meadowbrook reef trend of central Alberta, Canada (Amthor *et al.*, 1993). We also tested our preparation technique on synthetic calcite single crystals grown from a Ca-Cl-NH_4-CO_3 solution (Paquette and Reeder, 1990).

Powdered samples or individual crystals were embedded in a low-viscosity resin following the procedure described by Vali and Hesse (1990). The embedding blocks were trimmed to a cutting face 200 × 300 μm in size, oriented with respect to the faces of edges of the crystal selected for investigation. Ultrathin sections (700–800 Å) were cut from the block with a LKB ultramicrotome and a Diatome diamond knife, using $CaCO_3$-saturated H_2O to minimize dissolution of the carbonate phase. However, some reaction between the carbonate and the fluid used during sample preparation cannot be ruled out. Several consecutive ultrathin sections cut from the same block were selected and transferred onto TEM grids with a support film as a substrate.

Dissolution experiments were caried out by treating ultrathin sections directly on TEM grids with 0.01N HCl (pH ~ 2) solutions at room temperature for 2–20 seconds. One μL of solution was transferred onto the grid held with tweezers under the stereomicroscope. The excess solution was removed with filter paper.

TEM imaging, selected-area diffraction (SAD) and semiquantitative analysis were performed using a JEOL 100 CX equipped with an energy-dispersion X-ray detector (PGT IV, analyzable area 100 nm^2) operated at 100 kV, with imaging conditions of underfocus (100–300 nm). To minimize analytical errors due to electron irradiation (Van Tendeloo *et al.*, 1985), selected areas were analyzed only once, for 30 seconds.

Results and discussion

In synthetic calcite single crystals, a microcleavage is developed uniformly throughout 104 growth sectors and evidence of dislocations is scarce. In contrast, dolomite cement crystals show numerous microfracture-like features, interpreted to represent dislocations, oriented at high angle to the original $(10\bar{1}4)$ growth surface. The lamellar microfabric defined by microcleavage in 104 sectors is locally interrupted by massive lenticular cleavage-free domains. AEM analyses show a slight Mg-enrichment in these domains relative to the $10\bar{1}4$ sectors. In some cases, the orientation of the lamellar fabric changes sharply at the edge of a massive domain, forming a ramp-like feature. We tentatively interpret these massive domains as distinct growth sectors on facets (angular measurements are consistent with a $(10\bar{1}1)$ orientation) developed at macrosteps during crystal growth. These features could represent an early stage in the development of $10\bar{1}1$ arcuate slivers such as those detected by cathodoluminescence microscopy in diagenetic calcian dolomite by Fouke and Reeder (1992). The crystals described by Fouke and Reeder (1992) showed curved concentric zoning. Our observations suggest that the development of sector zoning at macrosteps during crystal growth of dolomite may lead to compositional heterogeneity even in crystals displaying planar $\{10\bar{1}4\}$ faces under the microscope.

TEM observations after treatment with 0.01N HCl show selective dissolution along microcleavage planes and along the dislocation-like features. The massive, cleavage-free domains are more resistant to etching (as would be expected if they consist of more stoichiometric growth sectors within a calcian dolomite). AEM analyses after etching show preferential loss of Ca over Mg. Minor amounts of Si and Al are also detected in many diagenetic dolomite crystals but do not seem associated with specific second-phase inclusions. Contamination during sample preparation cannot be ruled out at the moment. Noticeable losses of Si also result from HCl treatment.

Conclusions

TEM studies of carbonate ultrathin sections prepared by ultramicrotomy offer an alternative to the ion-thinning technique. The microcleavage induced during sample preparation overprints but does not mask features that are presumably inherited during crystal growth (dislocations, macrosteps and associated sectors showing compositional zoning). Dolomite is considered to be relatively unreactive under earth-surface conditions but the high resolution of TEM enables imaging of incipient stages of dissolution. AEM data must be evaluated cautiously because of its semiquantitative nature but it offers the potential of correlating intracrystalline compositional heterogeneity with growth features at the nanometer-scale. Ultramicrotomy complements the ion-thinning technique. An combined approach may lead to a better understanding of the nature and reactivity of carbonates.

References

Amthor, J.E., Mountjoy, E.W., Machel, H.G. (1993) *Bull. Can. Petrol. Geol.* **41**, 164–85.

Fouke, B.W. and Reeder, R.J. (1992) *Geochim. Cosmochim. Acta*, **56**, 4015–24.

Paquette, J. and Reeder, R.J. (1990) *Geol.* **18**, 1244–7.

Vali, H. and Hesse, R. (1990) *Amer. Mineral.* **75**, 1445–8.

Van Tendeloo, G., Gronsky, R.R. and Wenk, H.-R. (1985) *Phys. Chem. Minerals*, **12**, 333–41.

Wenk, H.-R., Barber, D.J., and Reeder, R.J. (1983) Microstructures in carbonates. In *Rev. in Mineral.* **11** (R.J. Reeder, ed.), 301–67. Mineral Soc. America.