

# Hydrolytic weakening of jadeite in UHP jadeite-quartzites from the Dabie Mountains, eastern China

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## ABSTRACT

Deformed jadeite grains in the UHP jadeite-quartzites from the Dabie Mountains, eastern China show evidence (by transmission electron microscopy, TEM) of plastic deformation: free dislocations, dislocation loops, dislocation networks, dislocation arrays and regularly spaced subgrain boundaries by dislocation walls. Electron energy-loss spectroscopy and TEM studies reveal the existence of water-rich bubbles within dislocations and imply a relationship with water-defect dislocation by water weakening in the jadeites. These observations suggest that the water-rich bubbles are a major weakening effect facilitating plastic deformation of jadeite by dislocation creep.

**KEYWORDS:** water-rich bubbles, water weakening, deformation mechanism, natural jadeite, Dabie Mountains, China, TEM, EELS.

## Introduction

DURING the past two decades, evidence for ultra-high pressure (UHP) metamorphism, such as the presence of coesite and diamond in eclogites, jadeite-quartzites and gneisses has accumulated (e.g. Chopin, 1984; Smith, 1984; Okay *et al.*, 1989; Sobolev and Shatsky, 1990; Xu *et al.*, 1992; Yang *et al.*, 1993; Su *et al.*, 1996). Some protoliths of reported UHP metamorphic rocks are of sedimentary origin (Chopin, 1984; Kienast *et al.*, 1991; Xu *et al.*, 1992; Wang and Liou, 1993; Schreyer, 1995; Shatsky *et al.*, 1995; Su *et al.*, 1996). Those UHP metasedimentary rocks of supracrustal origin record important information about the subduction and exhumation of continental crustal rocks. Clinopyroxene is a major phase in the lower crust and mantle and strongly influences the rheological properties of UHP metamorphic rocks. There has been extensive research on the deformation mechanisms of omphacite (e.g. Van Roermund and Boland, 1981; Boland and Tullis, 1986; Van Roermund,

1984, 1992; Godard and Van Roermund, 1995; Abalos, 1997; Bascou *et al.*, 2001; Mauler *et al.*, 2001; Brenker *et al.*, 2002), and diopside (e.g. Ave Lallemand, 1978; Stalios *et al.*, 1988; Raterron and Jaoul, 1991; Raterron *et al.*, 1994; Ingrin *et al.*, 1991, 1992; Buatier *et al.*, 1991; Dimanov *et al.*, 2003). Results available in the literature indicate that multiple dislocation glide and/or climb, grain-boundary mobility and mass-transfer processes are the dominant deformation processes involved in plastic deformation of omphacite (Van Roermund, 1992; Godard and Van Roermund, 1995). Experiments performed on clinopyroxene indicate that clinopyroxene-rich rocks deform more readily in the presence of water than under dry conditions (Boland and Tullis, 1986; Jin *et al.*, 2001; Bystricky and Mackwell, 2001; Dimanov *et al.*, 2003; Chen *et al.*, 2006). However, there is not much research on the deformation mechanism of jadeite itself (Stockert and Renner, 1998). Here, using observations from transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS), we discuss the deformation mechanisms of natural jadeite in the Dabie Mountains, eastern China.

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### Sample description and methods of study

The jadeites studied here (sample 92403) were collected in the UHP jadeite-quartzite zone from the Qianshan area of the Dabie Mountains, eastern China (Fig. 1 of Su *et al.*, 1996, 2004). The rocks are characterized by a shape-preferred orientation of jadeites and garnets (Fig. 1a) and are associated with retrogressed gneisses (Fig. 1b). The jadeite-quartzite is composed of quartz (45–55%), jadeite (35–45%), garnet (6%) and minor coesite, rutile, zircon and apatite (Fig. 1c). Jadeites range in size from 0.8 to 4.0 mm; garnet and quartz are finer grained (0.5–2.5 mm). Petrological and mineralogical investigations have indicated a complex polyphase history, with three main metamorphic stages (Cong, 1996; Su *et al.*, 1996; Liou *et al.*, 1997; Su, 2000): (1) peak UHP metamorphism is characterized by the mineral association: jadeite + garnet + coesite + rutile + apatite. Metamorphic *P-T*

conditions are estimated at  $\geq 28$  kbar and  $660 \pm 40^\circ\text{C}$ , with the presence of coesite in jadeite and garnet (Liou *et al.*, 1997; Su *et al.*, 1996). (2) An early retrograde stage involves the polymorphic transformation of coesite to quartz aggregates during decompression. It is characterized by the formation of early retrograde minerals: aegirine + diopside + garnet + glaucophane + quartz + rutile + magnetite. (3) A symplectite stage in which, in some samples, jadeites and garnets have been replaced by a symplectitic assemblage of amphibole + plagioclase, indicative of amphibolite-facies retrogression at 8–10 kbar and  $550\text{--}600^\circ\text{C}$  (Liou *et al.*, 1997; Su, 2000).

In the thin section of the XZ structural plane, elongated crystals of jadeite as well as garnet and quartz underline the foliation (Fig. 1d). This orientation is also recognizable in hand specimen and at the outcrop scale (Fig. 1a). The jadeite average aspect ratio is  $X:Y = 3.01$ ,  $Y:Z = 2.98$ ,

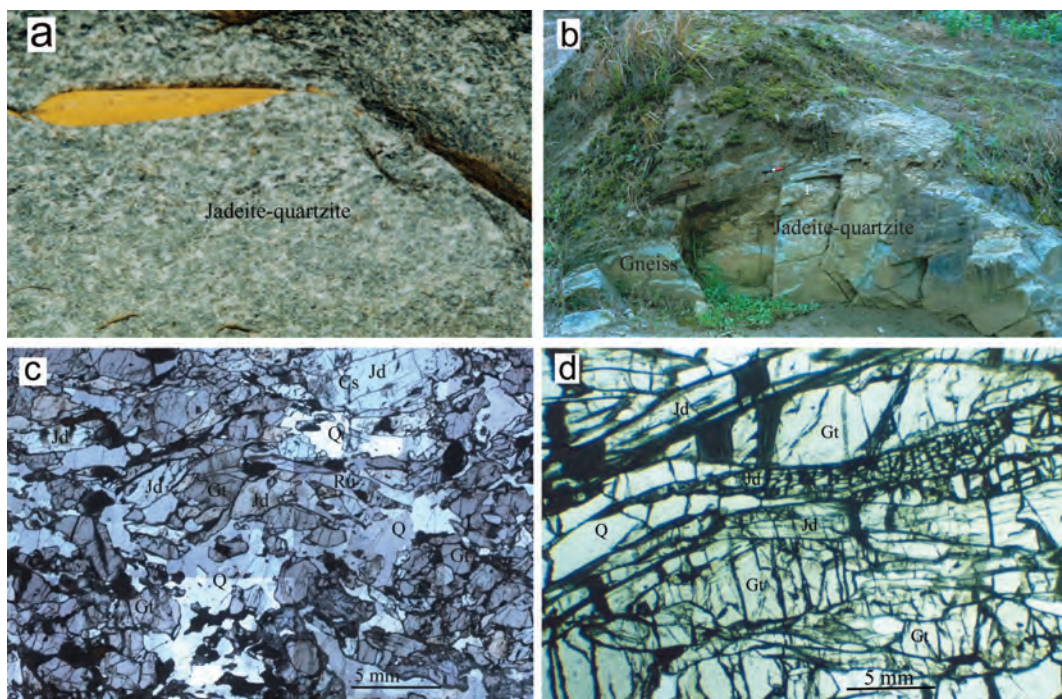


FIG. 1. Photos of jadeite-quartzite from the Dabie Mountains: (a) jadeite-quartzite from the Qianshan area shows shape-preferred orientation; (b) jadeite-quartzite occurs as layers in association with retrogressed gneisses from the Qianshan area. The jadeite here is strongly deformed; (c) photomicrograph of a jadeite-quartzite (in the YZ structural plane) composed of quartz, jadeite, garnet and minor coesite, rutile and retrograde metamorphic minerals. Sample No. 92403; (d) photomicrograph showing strongly elongated jadeite and garnet grains in the XZ structural plane of jadeite-quartzite, sample No. 92403.

X:Z = 5.33, and the Flinn coefficient,  $K = 1.01$ . Deformed jadeites show some undulatory extinction features, which are characteristic of deformation by dislocation creep.

Doubly polished thin sections with a thickness of 0.02–0.03 mm were prepared from foliated jadeite-quartzites (92403). Clean jadeite foils were then prepared from the thin sections and glued onto the copper rings of TEM grids. The jadeite foils were prepared by ion milling using a Gatan 600 until electron transparency was achieved. The TEM and EELS analyses were carried out using an HITACHI H8100 TEM and a JEM-2010F, respectively, with an acceleration voltage of 200 kV. The EELS analysis used

0.2 nm and 0.4 nm spectrometer apertures for hydrogen and oxygen, respectively.

## Results and discussion

### TEM observations

The TEM observations include a variety of dislocation substructures in the jadeite grains (Fig. 2): free dislocations, dislocation loops, dislocation walls and dislocation arrays. The dislocation arrays (Fig. 2a) can be interpreted as tilted subgrain boundaries while the dislocation networks (Fig. 2b) imply an activation of more than two active slip systems (Ji *et al.*, 2003). Subgrain boundaries composed of dislocation

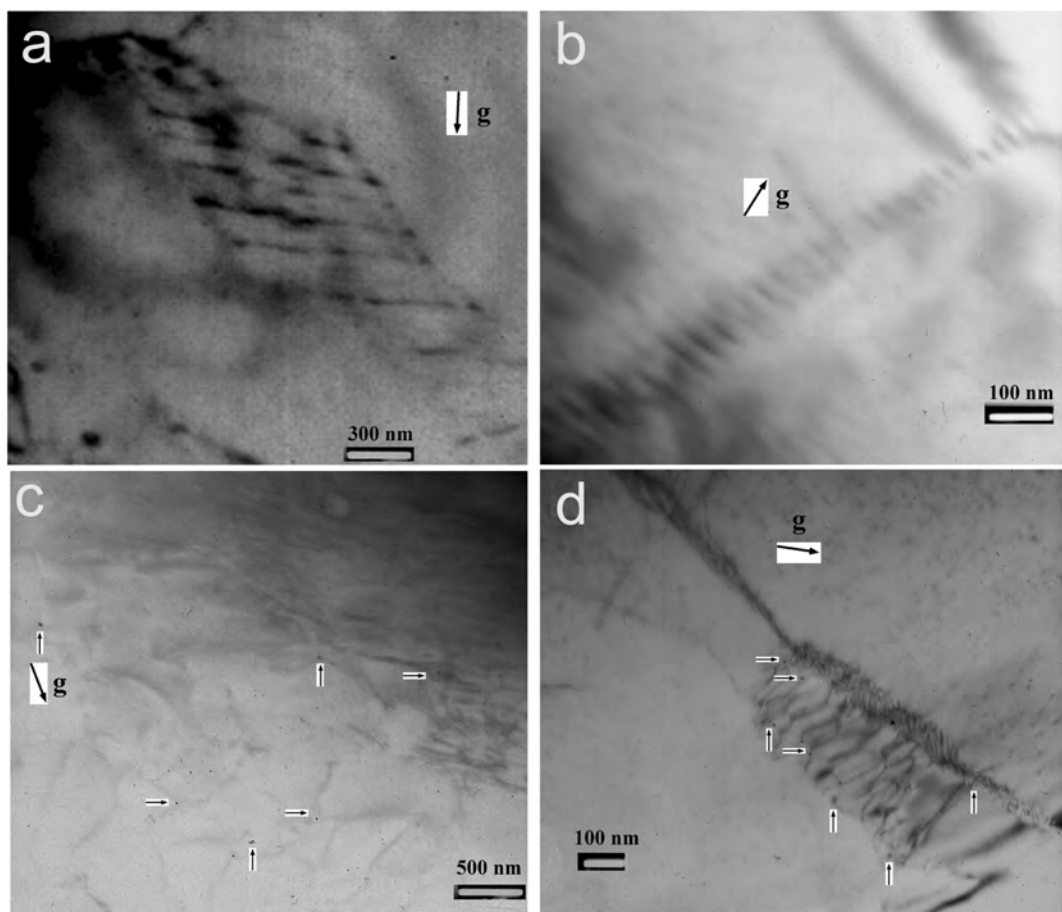


FIG. 2. Bright-field electron micrographs showing dislocations in the naturally deformed jadeite. Sample No. 92403. (a) Dislocation arrays form a subgrain boundary,  $g = 110$ ; (b) free dislocations and dislocation walls,  $g = 333$ ; (c) dislocation tangle, dislocation walls and dislocation loops with a few bubbles,  $g = 002$ ; (d) dislocation loops, connected to one another via a common bubble,  $g = 400$ .

arrays and locally, dislocation walls and dislocation loops, are extensively developed. Subgrain sizes (2–6  $\mu\text{m}$ ) appear to be irregular and contain a low density of free dislocations ( $8.31 \times 10^7 \text{ cm}^{-2}$ ). The subgrain boundaries in the jadeite indicate that dislocation climb is more efficient under hydrous conditions. The dislocation junctions are complex intersections of several dislocations (Fig. 2c–d). Free dislocations may have interacted to form nodal points or junctions (Fig. 2c), others are curved or form loops (Fig. 2d). The presence of dislocation junctions indicates that dislocation interactions and consequently the operation of multiple slip systems took place in the deformed jadeite grain (Voegelé *et al.*, 1998; Wang and Ji, 1999). The microstructure observed in the jadeite grains indicates that a dislocation creep mechanism occurred. Transmission electron microscopy also recognizes a few bubbles within dislocation loops of the jadeite (Fig. 2c–d).

#### EELS analysis

In order to further check the composition of the bubbles in the jadeite (Fig. 2c–d), an EELS analysis of the same jadeite was also recorded from the bubbles (Fig. 3). The existence of water molecules within jadeite is further confirmed by EELS measurements. Figure 3 shows three peaks, which are consistent with hydrogen and oxygen, respectively ( $\sim 12.5 \text{ eV}$  for hydrogen and 540 and 566 eV for oxygen) (Ahn and Krivanek, 1983). Clearly it indicates that the bubbles consist of water molecules.

A bubble is  $\sim 300 \text{ \AA}$  in size within the dislocation loops (Fig. 2c–d). We noticed that there are the water-rich bubbles with dislocation loops attached to them in the jadeite grain (Fig. 2d). The bubbles sometimes form bead-like strings and some loops are often connected to one

another via a common bubble. Clearly, the effect of water-rich bubbles on dislocation creep of jadeite is significant.

It is important to note that jadeite can accommodate significant amounts of interstitial H under UHP conditions by both in experimental studies (Bromiley and Keppler, 2004) and studies of the jadeite from the same quartzite (Su *et al.*, 2004). Under peak metamorphic conditions in a subduction-zone setting, it is entirely probable that jadeite grains contained considerable H, possibly close to saturation values. This provides the necessary source required for bubble formation and growth. In other words, with the presence of water, point defect associates can be formed by combining (OH)–O and vacancies (Kohlstedt *et al.*, 1996). Bubble formation can be linked to clustering of H defects in the host phase. A possible point defect associate is formed by 4H replacing Si and may be important in quartz (McLaren *et al.*, 1983) and olivine (Beran and Putnis, 1983). In quartz, McLaren *et al.* (1983) proposed that large-scale clustering of these 4H groups results in the formation of a water bubble. Increase in the bubble volume (and further clustering of H defects) would speed up dislocation motion by diffusion of Si and O away from the bubble site into a linked edge dislocation loop and H diffusion towards the bubble (McLaren *et al.*, 1983), thus enhancing the defect mobility and dislocation climb velocity (Hobbs, 1984). The water pressure in the bubbles increases and sessile dislocation loops are nucleated to relax this inner pressure and to allow water precipitation to continue (e.g. McLaren *et al.*, 1983, 1989; McLaren, 1991; Mackwell *et al.*, 1985). The sessile dislocation loops bound an extra half plane formed by the jadeite grain removed from the bubble surface. The process of bubble growth is, therefore, linked to two separate diffusion processes (i.e. Si + O,

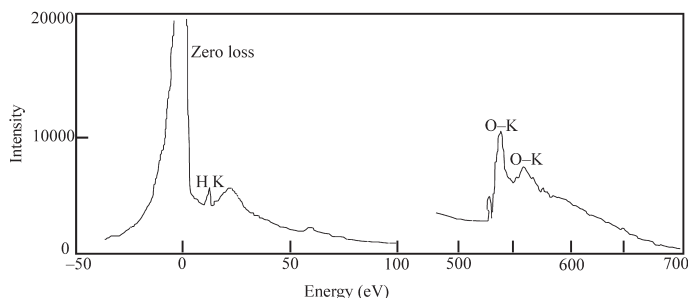


FIG. 3. EELS spectra of a bubble within the deformed jadeite (sample No. 92403).

and H). However, the mechanism for incorporating H in jadeite is actually quite complex. Bromiley and Keppeler (2004) showed that H is probably incorporated close to O–O edges adjacent to both *M1* and *M2* sites. Skogby and Rossman (1989), Skogby *et al.* (1990), and Skogby (1994) found a positive relationship between the trivalent ions ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ) and OH concentration in pyroxenes by both natural and synthesized pyroxenes. Many studies of natural jadeite and omphacite samples (e.g. Smyth *et al.*, 1991; Su *et al.*, 2004) have highlighted the role that *M2* vacancies could play in terms of charge-balancing, and providing a mechanism for, H incorporation. The compositional zone or transition from the *C2/c* of jadeite to the *P2/n* of omphacite and coronal textures in the jadeite of the jadeite-quartzite, suggest significant enhancement of grain-boundary migration by  $\text{H}_2\text{O}$ . OH in the jadeite would liberate  $\text{H}_2\text{O}$  during its exhumed process (Su *et al.*, 2004). It appears that the presence of small quantities of water have a major weakening effect on plastic deformation within the dislocation regime of the jadeite grains. Studies on the concentration levels of hydroxyl in nominally anhydrous upper mantle minerals demonstrate that clinopyroxene incorporates more hydrogen than the other phases, i.e. the OH contents of clinopyroxene > olivine > garnet (Ingrin and Skogby, 2000). Therefore the water-weakening effect is much more significant for clinopyroxene than other minerals such as olivine and even plagioclase (Chen *et al.*, 2006) during subduction-related processes.

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