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LETTER

The acoustic emissions signature of a pressure-induced polytypic transformation in chlorite

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ABSTRACT

We present results of an acoustic emissions (AE) study of single crystals of chromian-clinochlore during compression to 10 GPa at room temperature. Distinct AE are detected associated with the type Ia → Ib transition at 6 GPa. Analysis of AE source locations and first motions at transducers are consistent with a rapid collapse of the *c*-axis of the sample and AE originating within the sample and not the surrounding pressure medium. This is the first time that AE have been detected directly from a phase transformation in the multi-anvil press and opens new possibilities for kinetic studies and studies of deep-seismogenesis.

Keywords: High-pressure studies, mechanical properties, new technique, chlorite

INTRODUCTION

Oceanic crust becomes highly hydrated during its passage from spreading ridge to subduction zone. Within the greenschist facies, chlorite commonly develops as a hydrous mineral of the MORB component of the crust (e.g., Banerjee and Gillis 2001). During subduction this chlorite undergoes structural rearrangements in response to the increased confining pressure and, at high temperatures, transforms to amphibole-bearing assemblages. However, in subduction zones with low thermal gradients, a recent experimental study (Fumagalli and Poli 2005) indicates that chlorite transforms to assemblages containing the "10-Å phase," a mono-hydrated sheet silicate with interlayer H_2O. There is also evidence for a nearly polymorphic high-pressure transformation between lizardite and chlorite (Dódony and Buseck 2004). Chlorite also undergoes a pressure-induced reversible polytypic transformation at 6 GPa and 298 K (Welch and Crichton 2005), and the IIb polytype undergoes anomalous transformational behavior at 9 GPa and 298 K that involves exceptionally large positive increases in the vibrational frequencies of hydrogen-bonded OH groups (Kleppe et al. 2003; Welch et al. 2004). Thus, a rich variety of transformations between sheet silicates could occur in cooler subduction zones. These transformations can involve small, but potentially significant, volume changes. If the transformational behavior is sufficiently rapid (negligible hysteresis), it might contribute to the mechanisms of subduction-related seismicity.

Here we report results of a multi-anvil acoustic-emission study of the 6 GPa polytypic transformation Ia → Ib in Type-I chlorite (Welch and Crichton 2005). This transformation is rapid and reversible.

METHODS

Crystals of chromian-clinochlore from Erzincan, Turkey were taken from the same hand specimen as that of Welch and Crichton (2005), who reported a chemical composition (anhydrous) of $Mg_{4.93(4)}Cr_{0.77(5)}Fe^{3+}_{0\,1.1(3)}Al_{1.20(2)}Si_{2.96(5)}O_{14}$. Two inclusion-free, unfractured, tabular crystals of good optical quality were chosen, having dimensions approximately 1.5 × 5 × 5 mm with the *c*-axis being parallel to the short dimension. Each crystal was packed in a semi-sintered MgO octahedral cell of 14 mm edge-length. Crystals were placed in the cell such that the normal to (001) was coincident with a threefold axis of the cell and off-centered along this axis by approximately 1 mm. An internal pressure calibrant consisting of Bi -foil was placed in the MgO cell in a symmetrically equivalent position with the sample. A schematic section of the cell arrangement is presented in Figure 1. The Bi I-II (2.25 GPa) and Bi III-V (7.7 GPa) transformations were detected by changes in the electrical conductivity of the foil and used to calibrate the cell pressure against press load. We estimate that the precision of pressures interpolated from these fixed-points is better than 0.1 GPa. The MgO cell was compressed by 8 tungsten carbide anvils with 8 mm truncations in a standard 6–8 double-stage multi-anvil geometry (Kawai et al. 1973) using the 1000 tonne press at University College London.

Acoustic emissions (AE) were monitored using an 8-transducer system developed from the technique described by Dobson et al. (2004). Lead-zirconia titanate transducers were used with a 5 MHz resonant frequency and 1/4-wavelength backing plates. These transducers, which had a flat response to P-waves across the 1–5 MHz frequency range, were bonded onto truncations on the back corners of all 8 anvils and connected to a Vallen high-speed AE recorder via programmable-gain pre-amplifiers. For all experiments reported here the gain was set to 35 dB. The Vallen system sampled waveforms at a rate of 10 MHz for each transducer; this

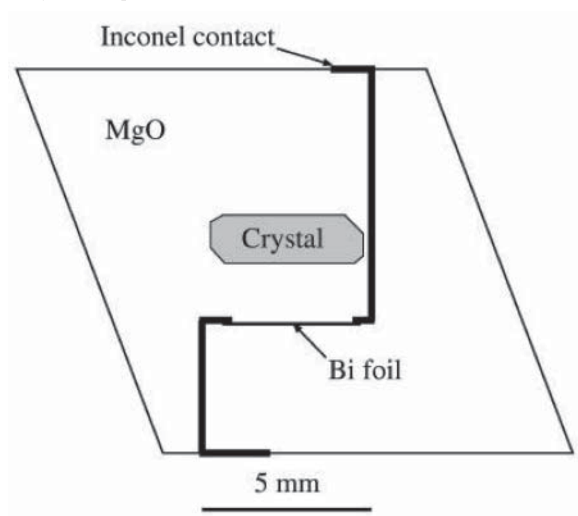

FIGURE 1. Schematic diagram of the high-pressure cell.

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sampling rate ensured that aliasing did not occur at the lower-frequency end of the transducer range where most of the energy was being radiated. Full waveforms were collected for each hit at each transducer. A sequence of individual hits at different transducers that can be reasonably located, given the known velocity structure of the sample and anvil assembly, is called an event. All of the hits in an event are assumed to originate from a single source at the point of location. We considered locations involving hits on four or more transducers to be a reliable criterion for defining an event. Thus AE sources that resulted in signals, which were detected at less than four transducers, contribute to the hit and energy statistics but are not registered as located events. Microseismic events comprising hits at 4 or more transducers were located in the cell using a non-iterative analytical location algorithm which is part of the Vallen "Visual AE" software suite. First arrivals were picked manually for determining first motions at each transducer. Full details of the new 8-transducer system will be presented elsewhere.

RESULTS

Acoustic emission energy-rates and hit-rates detected during compression to 9 GPa are presented, together with the resistance of the Bi calibrant, in Figure 2. The Bi I-II (2.25 GPa) and III-V (7.7 GPa) transitions produced clear reductions in resistance of the Bi -foil and provided an internal pressure calibration for this experiment. Multi-anvil assemblies are noisy during initial compression (e.g., Dobson et al. 2004). However, as the void space is compressed out of the cell and the gaskets are formed, the bulk of which occurs at pressures between 1 and 2 GPa, system noise decays exponentially, becoming negligible by about 4.5 GPa (approximately 10 500 s). There is then a region of increased AE activity, seen in both AE energy and hit-rate, between 13 500 and 15 000 s.

Figure 3 presents AE data for the 11 000–17 000 s interval re-plotted against sample pressure, as interpolated from the Bi-calibration points. The precision in the interpolated pressure in this experiment is approximately 0.1 GPa. The increase in AE activity occurs from 5.9 to 7.7 GPa, closely coinciding with the pressure-range of transformation observed by X-ray diffraction. Welch and Crichton (2005) observed reflections from both high-pressure and low-pressure phases between 5.9–7.1 GPa. Furthermore, the region of increased AE activity starts with a pulse of high-energy events followed by a rapid increase in hit-rate and subsequent gradual decay in both hit-rate and energy-rate (a third of the AE energy detected during transformation is radiated during the first 0.3 GPa of transformation). This can be interpreted as arising from a rapid onset of transformation resulting in initial high strain events followed by a subsequent more sluggish completion of transformation and/or rearrangement of the pressure medium around the reduced volume of the sample. A duplicate experiment produced a similar increase in AE activity at approximately 6 GPa, but failure of the Bi foil at around 5 GPa precluded accurate calibration of sample pressure against press load. Therefore, we only present data from the one well-calibrated experiment here, but recognize that transformational behavior was registered in both experiments at similar pressures.

The interpretation of the AE energy and hit-rate statistics as related to strain within the sample is further strengthened by locations of AE sources, which occurred during transformation (Fig. 4a). Although some 4000 AE signals (4000 hits) arrived at individual transducers in the 5.9–7.7 GPa pressure range, these hits produced only around 100 located events. This is due to the stringent criterion for locations described above. AE sources which resulted in signals, which were detected at less than four transducers, contribute to the hit-rate and energy-rate statistics, but are not registered as located events. The located events in Figure 4a are superimposed upon a reflected-light micrograph of the recovered and sectioned cell and projected onto the plane of the micrograph. Solid symbols are for AE events occurring at pressures of between 5.9 and 6.5 GPa and open symbols are for events between 6.5 and 7.7 GPa. For comparison, located events during the time-period 7000–9000 s (no transformation, but a similar total number of hits) are plotted in Figure 4b and locations from an experiment with only a solid MgO pressure medium (no sample) in Figure 4c. The localization of events to within the sample during transformation is obvious when compared to the locations of background events away from the transformation pressure. Despite relatively large formal location errors (approximately ±10 mm), AE sources are consistently located to within the sample during transformation, but not at other times. There is some localization in the MgO pressure medium immediately

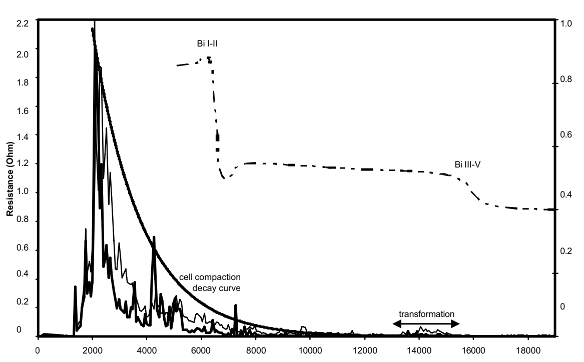

FIGURE 2. Plot of AE energy-rate (bold solid line) and hit-rate (faint solid line), and resistance of Bi-foil (dashed line) during compression of chromian-clinochlore to 9 GPa. The changes in resistance associated with the Bi I-II (2.25 GPa) and Bi III-V (7.7 GPa) transitions are labeled. The noisy initial compaction of the cell is apparent, as is the exponential decay in cell noise (bold solid curve fitted to the AE statistics). The region of AE associated with transformation is arrowed.

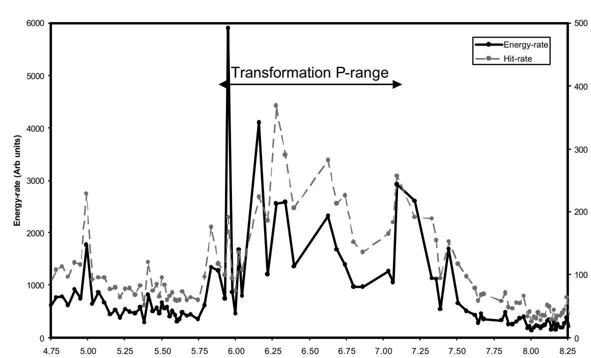

FIGURE 3. Plot of AE energy-rate and hit-rate against cell pressure. The pressure range over which transformation was observed by single-crystal X-ray diffraction is marked. AE energy is indicated by the solid line; hit-rate is plotted in a broken line.

TABLE 1. Manually picked first motions at each transducer for located events during the transformation

Transducer	Angle to (001)* (°)	–Ve first motions†	+Ve first motions†	Total picks
1	90	5	1	6
2	90	21	8	29
3	+19.5	4	2	6
4	–19.5	20	9	29
5	+19.5	5	5	10
6	–19.5	17	8	25
7	+19.5	8	4	12
8	–19.5	12	10	23‡
		% –Ve	% +Ve	Total
90° to (001)	74.3	25.7	35	
19.5° to (001)	62.8	36.2	105	

* The angle between the (001) basal plane of the crystal and a line from the center of the cell to the transducer.
† Negative first motions indicate a compression of the source region in the direction of the transducer and positive first motions indicate a dilation of the source in the direction of the transducer.
‡ We were unable to assign a clear first motion value to one arrival on this transducer.

surrounding the sample seen in Figure 4b compared with the MgO cell. This might be due to differences in strength between the sample and MgO pressure medium, which cause increased differential stresses at the interface between the two. However, AE sources during the transformation are much more strongly localized into the sample volume than at any other time.

The type I*a* to type I*b* transformation in chlorite involves a volume reduction of around 2%, which is due almost entirely to contraction of the *c*-axis (Welch and Crichton 2005), primarily reflecting contraction of the interlayer space. It is, perhaps, surprising that such a clear signal for this transformation, corresponding to a total shortening of the crystal of just 20 μm is registered in our experiments. Furthermore, first motions of transducers for hits associated with the transformation can be used to indicate the orientation of strain in the source region. A simple statistical analysis of first motions is presented in Table 1. Acoustic emissions originating from within the sample should display dominant negative first motions at transducers oriented normal to the silicate sheets of the sample and little compressive-wave energy should be radiated in other directions.

This is consistent with the dominantly negative first motions in transducers oriented along the axis of the cell, normal to the basal plane of the sample, and the weaker dominance of negative first motions in transducers oriented at 70.5° to the axis of the cell. By contrast, if AE originated from cell relaxation around the transformed crystal they should have predominantly negative first motions in transducers along the cell axis and positive first motions in transducers at 70.5° to this axis. In addition, if

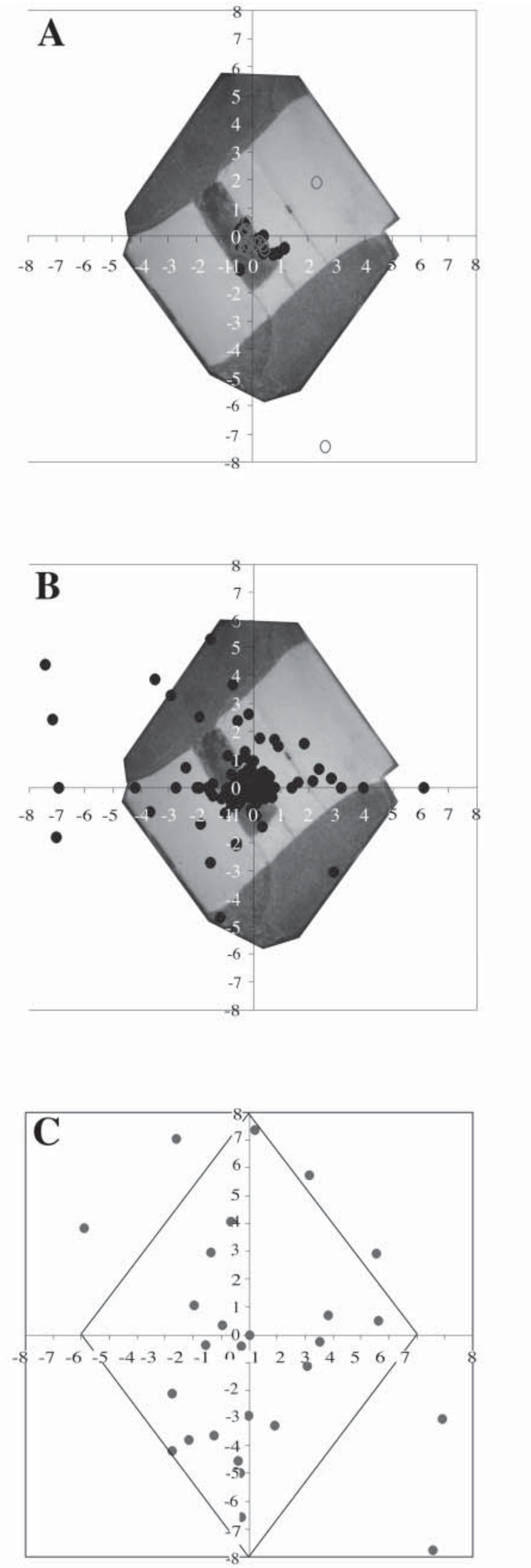

FIGURE 4. Source locations of AE during transformation (**a**) and outside of the transformation pressure range (**b**). The locations presented in **c** are for a solid MgO cell with no sample during compression from 1 to 6 GPa. Locations are overlaid on an optical micrograph of the sectioned recovered cell and projected onto the plane of the section. Only locations less than 4 mm away from the plane of the section are plotted since this includes the entire pressure medium and little else. The scale is in millimeters. Closed symbols in **a** are for the pressure interval 5.9–6.4 GPa and open symbols in **a** are for the interval 6.4–7.5 GPa.

the observed AE originated in the pressure medium they should be located within a cylinder or annulus surrounding the sample, rather than tightly clustering towards the center of the sample.

Discussion

Phase transitions, such as those in chlorite, can generate detectable acoustic emissions in multi-anvil experiments. This proof-of-concept study demonstrates the utility and potential of multi-anvil AE techniques for monitoring phase transitions. In particular, the continuous nature of AE monitoring might prove useful in kinetic studies when combined with diffraction studies, which necessarily interrogate the sample in discrete time steps.

Chlorite is an important constituent of subducting slabs where rapid phase transformation associated with conditions of increasing pressure and temperature might contribute to seismogenesis. The first motions detected here are not consistent with double-couple events, which dominate the focal mechanism solutions of intermediate depth earthquakes. However, it has been suggested that hydration of the slab can occur preferentially along preexisting fault planes (Peacock 2000). Transformation of hydrous phases involving a rapid, but not necessarily large, reduction in volume within these faults might sufficiently reduce the effective stress normal to the fault surface to initiate its remobilization.

Acknowledgments

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