Halide based shock-wave treatment of fluid-rich natural phases

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Abstract. For the synthesis of high pressure phases from natural minerals and the shock wave treatment of fluid bearing phases a halide based method was developed. The experiments were performed in the pressure range between 25 and 162 GPa with a success rate for the new method of 100% for the new method. Based on the Impedance Corrected Sample Recovery Capsule under avoiding the adiabatic decompression a direct comparison between different loading paths and sample holder geometries is possible. The recovered samples show neither indications of melting in the case of kaolinite and very limited degassing in the case of carbonates. The recovery of amorphous water bearing Al–Si-phases with Aluminum in four-, five- and six-fold coordination was possible. The samples were analyzed with scanning electron microscopy, x-ray diffraction, nuclear-magnetic-resonance- and infra-red-spectroscopy and the results were directly compared.

1. Introduction

For geological processes, involving high-pressure (e.g. subduction) fluid phases in minerals plays a very important role. This includes for example the incorporation of water into HP-phases like wadsleyite and ringwoodite [1]. In subduction processes in recent times the possibility of the so called “core sedimentation” [2] of subducted and folded oceanic slabs at the core-mantle boundary is under discussion [3].

Because these subducted slabs consists of serpentinized oceanic crust with minor components like calcite, celadonite, iron oxyhydroxides and trace pyrite [4] fluid phases (H₂O, CO₂) will have large influence not only on the melting behavior of these slab. The successful synthesis of HP-phases with the coexistence of CO₄–SiO₆-structures [5], the synthesis of phases with unexpected stoichiometries [6] and the synthesis of [C₃O₉]⁶⁻-structures [7] indicate the possibility of a number of unknown phases with tetrahedral coordinated carbon to oxygen. These new discovered phases open new possibilities for the understanding of the deep carbon cycle.

On the other hand the synthesis of HP-phases with [CO₄]⁴⁻-structures with shock-wave methods is very difficult because all kinds of carbonates show a degassing behavior along the
Figure 1. Completely destroyed carbonate after shock wave loading, sample Cc1, 13 weeks after experiment. (a) SE-picture, enlargement at scale. (b) Ca-EDX-mapping. Enlargement compare with figure 1a.

Table 1. Experimental conditions and sample output (wt-%) of the performed experiments.

| sample-Nr. | method   | buffer-plate | figure in this work | p [GPa] | shock-temp. [K] | relative shock temp. [K/GPa] | adiabatic decompression | flyer plate thickness [mm] | sample output wt-% NaCl + Sample wt-% |
|------------|----------|--------------|---------------------|--------|----------------|-----------------------------|------------------------|-------------------------------|----------------------------------|
| K3         | reflection | no           | 3A                  | 162    | 6800           | 42                          | yes                    | 3                             | 75.02                          | 66.23                           |
| K4         | impedance | no           | 3A                  | 30     | 4000           | 134                         | partially              | 4                             | 75.05                          | 64.02                           |
| K5         | impedance | 1 mm Al      | 3B                  | 33     | 33             | 134                         | partially              | 4                             | 69.13                          | 22.57                           |
| K6         | reflection | no           | 3C                  | 103    | 4500           | 44                          | no                     | 4                             | 75.30                          | 34.44                           |
| Cc1        | impedance | no           | 3A                  | 25     | 3800           | 150                         | partially              | 4                             | 78.72                          | 70.58                           |
| Cc2        | impedance | 1 mm Al      | 3B                  | 33     | 33             | 460                          | partially              | 4                             | 78.07                          | 68.61                           |
| Cc3        | reflection | no           | 3C                  | 116    | 4600           | 40                          | no                     | 3                             | 69.84                          | 60.31                           |
| Cc4        | reflection | 1 mm Al      | 3D                  | 102    | 102            | 40                          | no                     | 4                             | 63.95                          | 48.82                           |

release path [8] (figure 1). For this reason a shock wave synthesis method for fluid bearing phases will be required able to work also in the pressure range \( p > 100 \) GPa under avoiding of degassing processes with the probability of complete sample recovery.

2. Experimental Methods
For all experiments the Impedance Corrected Sample Recovery System [9] under avoiding the adiabatic decompression of the sample powder [10] was used. The sample-impedance powder mixture was prepared with rock salt [11] instead of copper powder [12]. Sample materials were kaolinite KGa-2 [13] and synthetic calcium carbonate with vaterite structure. Four different experimental setups, derived from the commonly in Freiberg used system [14] were used. For the impedance method Cu-sample holders with a central pin were manufactured [15] and for the reflection method special Cu-capsules for W-reflectors and sample were developed (figure 2).

The complete arrangements of the experiments are given in figure 3. As reference material a copper-powder-kaolinite mixture was used (sample K3), prepared similar as in Keller 2012 [16] described. This sample undergoes furthermore an adiabatic decompression.

All rock salt bearing samples were statically precompressed before experiments took place.
They were executed in a glove box under nitrogen atmosphere to its technical density limit and for this reason the porosity in all experiments was assumed with 1.0. The rock salt:sample ratio was < 9 : 1 in any case. As buffer plate between flyer and container top aluminum discs were used with a diameter of 100 mm and 1 mm thickness (flyer plate diameter is 80 mm in all cases, flyer material is steel 1.4301). For experiments with buffer plate every time flyer plates with a thickness of 4 mm were used to ensure a sufficient number of reflections between buffer plate and container top. Therefor simultaneously enough time for the pressure-buildup in the sample is possible. For all experiments the flyer plate velocity was calculated with the MatLab-software package under using of the derived Gurney-equation for the open-face-sandwich-configuration [17]. The pressures were calculated with the material data after the database http://www.ihed.ras.ru/rusbank. For the experiments without buffer plate the temperatures were calculated after the scheme by Sharp [18] and for a better comparability of the experiments the relative temperature [K/GPa] [19]. In the case of experiments with buffer-plates currently a sufficient temperature calculation in not yet possible and still under development.

The recovered kaolinite samples were analyzed with $^{27}$Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR), infra-red (IR) spectroscopy, x-ray diffraction (XRD) and with field emission (FE) scanning electron microscopy (SEM), the carbonate samples currently only with SEM. All samples were analyzed two times, the first analysis before and the second after solving the sodium chloride with water ($3 \times$ in a supersonic cleaner with distilled water at 50 °C). The recovery process of the reference sample K3 follows Sekine [20].

The experimental conditions are given in table 1.

3. Results
3.1. Starting material
The kaolinite KGa-2 with a grain size of < 1 µm consists of tabular crystals (figure 4a). The XRD-measurement (figure 4d) shows the diffraction pattern of the reference material KGa-2 [21]. The $^{27}$Al-MAS-NMR (figure 4c) gives well ordered Al in six-fold coordination. The IR-spectra (figure 4c) of KGa-2 does coincide with the literature data [22] with peak list therein. The Ca-carbonate/ rock salt mixture consist on tabular or isometric Ca[CO$_3$]-crystals with excellent

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Figure 2. Sample holder for the reflection method. (a) Schematic cut section through the copper capsule with W-reflectors and sample. Thickness of all parts 1 mm. (b) W-reflectors in the Cu-capsule with sample piston (diameter of the W-reflectors 30 mm), diameter of the Cu-capsule and of the sample piston 34 mm. (c) Completed sample recovery capsule. (d) Sample recovery capsule after shock experiment (experiments Cc4, K6 and K7 in table 1).
cleavability and a grain size less than 20 \( \mu \text{m} \) (figure 4b). The small grain size of both types of samples indicates its usability for the following experiments while a complete embedding of the sample grains in the salt matrix is required (sample height before experiment 1 mm).

3.2. Reference material

In the reference experiment K3 the kaolinite shows completely amorphization and melting (figure 5a). In some cases the sample material encloses the Cu-grains with a protecting effect of the metal powder for nitric acid (figure 5b). This behavior made the \(^{29}\text{Si-MAS-NMR}\) and the IR-spectroscopy impossible. The \(^{27}\text{MAS-Al-NMR}\) shows a significant reduction of the Al-coordination number from 6 to 4 and 5 (figure 5c). These melting processes and miscibility with Cu-powder make this method for fluid rich phases inapplicable.

3.3. Experiments

3.3.1. Experiments without buffer plate

**Impedance method**  In the case of experiments without buffer plate the NaCl is often molten, by Cc1 with small carbonate inclusions (figures 6a and 6b). Nevertheless after solution of the rock salt both types of sample, kaolinite and carbonate are recoverable with similar crystal shape like the starting material and without indications of melting (figures 6c and 6d).
Figure 4. Starting materials. (a) Kaolinite KGa-2, grain size < 1 µm, SE-microphotograph, enlargement at scale. (b) Synthetic Ca[CO$_3$] with perfect cleavability, grain size < 10 µm, SE-microphotograph, enlargement at scale. (c) $^{27}$Al-MAS-NMR of KGa-2 with well ordered six-fold coordinated Al. (d) XRD-pattern of KGa-2. (e) IR-spectrum of KGa-2.

Reflection method In kaolinite bearing samples the rock salt is completely molten (figure 7a), but if Ca[CO$_3$] is present small cubic salt crystals behind carbonate grains indicate the lacking of complete melting (figures 7b and 7c). After solution in water the recovered samples are under SEM not distinguishable from the samples recovered after the experiments by impedance method (figures 7d and 7e) or, in the case of kaolinite, from the starting material. At this juncture melting of kaolinite did not occur.

3.3.2. Experiments with buffer plate

Impedance method In the case of experiment K5 partially unmelted NaCl is visible (figure 8a) and the carbonate is mechanically fractured and pressed into the salt matrix (figures 8b and 8c). Also large unmelted crystallites of rock salt does occur (figure 8d). The carbonate shows after solution of NaCl with water the originally crystal shape similar the starting material (figure 8e) and the kaolinite aggregates are not distinguishable from the starting material with SEM (figure 8f).
With common methods shocked reference sample. (a) Molten amorphous Si-Al-Phase. (b) Cu-grain, surrounded by molten amorphous sample. (c) $^{29}$Si-MAS-NMR-spectra of the sample and the starting material KGa-2 with increased four- and five-fold coordination, NMR-measurements 3 weeks after experiment.

**Reflection method** In these experiments only the kaolinite sample K7 was investigated together with its NaCl-Matrix. The rock salt was completely melted (figure 9a) with non-uniform sample distribution (figure 9b). Despite the complete melting of NaCl after solution of the salt matrix in water the recovered sample show similar crystal aggregates as the starting material KGa-2 (figure 9c). In the case of carbonate the grains are also recoverable. These grains show indications of partially melting, but without visible degassing effects.

3.4. XRD-, IR- and $^{27}$Al-MAS-NMR-investigations

The XRD-pattern shows a decrease of ordering with increasing pressure, this concerns especially the c-direction [23] of the samples (figure 10a), treated with the impedance method. With increasing pressure up to $p > 100$ GPa the amorphization does increase too. In spite of the using of NaCl as pressure medium in all cases traces of Cu-metal were observed ($2\Theta \approx 43$ and 50°). In the pressure range $p > 100$ GPa an $\text{Al}_2\text{O}_3$-phase transition into the $\text{Rh}_2\text{O}_3$(II)-type was not observed [24]. The sample K6 shows the lowest crystallinity (reflection method without buffer plate).

In the case of impedance method in the lower pressure range the IR-spectra (figure 10b) indicates good agreement with the data after Kikuchi [23]. In the pressure range $p > 100$ GPa the samples are amorphized with an overlay of the main SiO$_4$–AlO$_4$-vibration modes. Despite the extremely HP-HT-conditions these samples does contain also water molecules, visible at the broad absorption band at 3460 cm$^{-1}$. This band does coincide with OH-stretching of water in kaolinite after Madejov [22] at 3442 cm$^{-1}$ and the small band at 1640 cm$^{-1}$ does coincide with the according OH-deformation of water at 1640 cm$^{-1}$ (after Madejov at 1630 cm$^{-1}$). Additionally the samples K5, K6 and K7 show a new NO$_3$-peak at 1384 cm$^{-1}$ with its highest intensity in the sample K6.
Figure 6. Experiments with impedance method and without buffer plate. (a) Molten rock salt (sample Cc1) with position of carbonate grains, SE-microphotograph, enlargement at scale, 13 weeks after experiment. (b) Localization of the carbonate grains in the overview from figure 6a with comparison of the loci of some grains (enlargement is given in figure 6a). (c) Ca\([\text{CO}_3]\)\_crystal after solving with water with shape similar the starting material, 11 weeks after experiment. SE-microphotograph, enlargement at scale (d) Sample K4 after solving in water with structures similar the starting material, SE-microphotograph, 8 weeks after experiment, enlargement at scale.

4. Discussion

Because this method was especially developed for shock-wave-treatment of fluid rich phases at high \(p-T\)-conditions a complete sample recovery also of phases with a lower chemical stability, compared with nitrides and/or carbides, will be required. First indicator for lacking of degassing processes is the shape of the recovered sample crystals. In all eight performed experiments a sample recovery with a crystal size and shape similar the starting material was possible. The kaolinite samples show neither indications of melting processes and also the influence of degassing of the carbonate bearing samples is very limited. Currently the Freiberg Shock Wave Lab works with a success rate of 100 \% for this halide based method independent on the used \(p-T\)-conditions and the used method (impedance or reflection). This method is usable for \(\text{H}_2\text{O}\)-bearing silicates and also for carbonates and makes the synthesis of samples from 100 mg up to more than 1 gram per experiment possible.

The comparison of the experiments with and without buffer plate shows a significant reduced temperature for the second setup type, visible in the partially or complete lacking of rock salt
Figure 7. Experiments with reflection method and without buffer plate. (a) Molten rock salt, sample K6, kaolinite is here not visible. SE-microphotograph, enlargement at scale, 8 weeks after experiment. (b) Carbonate crystal in partially molten rock salt (white rectangle: section in figure 7c), incident shock from bottom, sample C3, SE-microphotograph, enlargement at scale, 13 weeks after experiment. (c) NaCl-crystallites from figure 7b, SE-microphotograph, enlargement at scale. (d) Recovered carbonate with crystal shape, SEM-microphotograph, enlargement at scale. (e) Recovered kaolinite sample, SE-microphotograph, enlargement at scale, 9 weeks after experiment.

melting (samples K5, Cc2), except for the sample K7. But also in this case a relative temperature reducing, compared with sample K6, is detectable. First indicator is the lowest crystallinity in the XRD-measurements of the sample K6 and the second additional NO$_3^-$-adsorption band in the IR-spectra. Because all samples were pre-compressed under nitrogen atmosphere filled vacuoles
Figure 8. Experiments with impedance method and with buffer plate. (a) Unmelted NaCl-crystals, experiment K5, SE-microphotograph, enlargement at scale, 9 weeks after experiment. (b) Mechanically fractured carbonate crystal in unmelted NaCl-matrix, experiment Cc2, SE-microphotograph, enlargement at scale, 11 weeks after experiment. (c) Ca-EDX-mapping from figure 8b. (d) Unmelted NaCl, experiment Cc2, SE-microphotograph, enlargement at scale. (e) Recovered calcium carbonate with crystal faces. SE-microphotograph, enlargement at scale, 11 weeks after experiment. (f) Recovered sample K5, SE-microphotograph, enlargement at scale, 9 weeks after experiment.

with nitrogen may occur in the NaCl-matrix. Under pressure conditions $p > 100$ GPa and high temperatures the kaolinite will lose some of its water (at this conditions as $O^{-}$ and $2H^{+}$) and oxygen will undergo a composition with N to nitride. Because the decay of H$_2$O will increase with
increasing temperature the intensity of the NO$_3$-adsorption band in the IR-spectra should be the highest at the maximum relative temperature at high pressures (sample K6). Furthermore the IR-spectroscopy shows the occurrence of water molecules also in the pressure range $p > 100$ GPa. This may be interesting for the treatment of H$_2$O-bearing phases (e.g. wadsleyite) [1]. The two HP-samples K6 and K7 shows the highest relative mass loss after elimination of salt with water (table 1). This indicates the possibility of chemical and structural changes associated with partially loss of fluid phases (e.g. water) also in a dense halide matrix in absence of sample melting.

Despite the large similarity of the samples under SEM-investigation, the structural difference between the kaolinite samples are very large. The synthesis products in the case of kaolinite for the impedance method does coincide with the description in the literature [23], in the pressure range $p > 100$ GPa an amorphous Si–Al-phase with Al in four-, five- and six-fold coordination was obtained.

With this new halide based method a new tool for the shock wave treatment of fluid rich phases was developed. On one hand the complete lacking of undesirable shock wave reflections and the avoiding of adiabatic decompression make shock wave experiments, performed with this method under different conditions with different loading paths, directly comparable and also reproducible. This method should be tested with halides with higher density (KBr, CsCl, CsBr)
Figure 10. Sample measurements for all described samples. (a) XRD-measurements, 9 weeks after experiment. (b) IR-measurements, 12 weeks after experiment. (c) $^{27}$Al-MAS-measurements, 13 weeks after experiment. The $^{27}$Al-MAS-NMR shows an increasing peak broadening and increasing Al with four- and five-fold coordinations with increasing pressure. This behavior indicates a loss on near-range ordering with increasing $p-T$-conditions. Higher Al-coordination numbers were not observed.

and with different container and flyer plate materials to enlarge the possible $p-T$-field for shock wave experiments.

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