Highlight and Breakthrough for the paper of Liu et al. (2019) #6805

Neither antigorite nor its dehydration is "metastable"

Revision 3 (20/02/2019)

Thomas P. Ferrand[1]

1: Earthquake Research Institute, University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-0032, Japan.

ferrand@eri.u-tokyo.ac.jp

(keep metadata here for editorial office)

Keywords: Antigorite, serpentine, metastability, dehydration, dehydroxylation, earthquake, DDST, dehydration-induced seismicity, subduction.

At confining pressures up to 6 GPa (200 km depth), antigorite is the most abundant hydrous phase in the mantle between 300 and 700 °C (Wunder and Schreyer 1997). Therefore, the dehydration of antigorite has been studied for decades as it is considered as the most probable trigger of earthquakes in the mantle of subducting slabs (10 to 40 km below the subduction interface; e.g. Peacock 2001; Hacker et al. 2003; Abers et al. 2013).

Liu et al. (2019) studied the kinetics of antigorite dehydration at 1 atm using non-isothermal thermogravimetric analysis, which allowed determination of activation energy variations as the reaction progresses (e.g. Trittschack et al. 2014; Wang et al. 2015). The results show that the dehydration consists of two dehydroxylation steps (Fig. 1), as is consistent with high-pressure experiments (Chollet et al. 2011). First, a slow dehydroxylation process breaks low-energy OH bonds; then, high-energy OH bonds are quickly broken, leading to complete antigorite breakdown. Similar experiments on chrysotile (Trittschack et al. 2014) and lizardite (Zhou et al. 2017) have also indicated multi-step reaction scenarios.

Liu et al. (2019) confirm the fast antigorite breakdown — a key factor for seismicity. Sudden stress transfers are likely to occur in the vicinity of dehydrating serpentinized faults, as recently demonstrated using laboratory analogues (Ferrand et al. 2017). The latter study, along with seismological observations (Cai et al., 2018; Bloch et al., 2018; Kita, and Ferrand, 2018) indicate that the lower Wadati-Benioff plane of the double-seismic structure does not correspond to the dehydration limit of antigorite, but rather to the hydration limit of the

oceanic mantle (Fig. 2). Furthermore, dehydration-induced earthquakes have been demonstrated experimentally for both > 0 and < 0 volume changes, which suggests that the earthquakes are triggered by dehydration itself while the resulted fluids are only a secondary factor.

Under subduction conditions, antigorite dehydration is not "seismic" (Chernak and Hirth 2010, 2011; Okazaki and Hirth 2016; Gasc et al. 2011). When a ratio of heating rate to strain rate typical for real slabs (100 – 10,000 K) is applied, antigorite-olivine mixtures undergo seismic events (Ferrand et al. 2017). Most likely, a dehydration-driven stress transfer triggers the earthquakes in fresh peridotite at the tip of dehydrating faults (Dehydration-Driven Stress Transfer model; Ferrand et al. 2017) whereas ductile deformation is dominant in serpentinites, as supported by experiments (Chernak and Hirth 2011; Gasc et al. 2011) and field observations (Scambelluri et al. 2017; Plümper et al. 2017).

Antigorite "metastability" was invoked to explain why its dehydration curve does not fully fit the lower plane of the double-seismic structure (Fig. 2; e.g. Peacock 2001). Part of this seismicity cannot be explained by antigorite dehydration (e.g. Abers et al. 2013), even considering various compositions and environments (Ferrand 2019). However, some experimental work demonstrated that, at pressures between 1 and 6 GPa (35 to 200 km), antigorite dehydrates quickly in the stability field of Fo + En + H_2O (above 600 to 700 °C), which suggests that subducting slabs do not contain "metastable" antigorite (Inoue et al. 2009; Ferrand et al. 2017).

In the MgO-SiO_2-H_2O system, antigorite has 12 ideal discrete compositions depending on P and T (Wunder et al. 2001), which makes it an atypical serpentine variety. Additional chemical variability (e.g. the FeO-Fe_2O_3-MgO-Al_2O_3-SiO_2-H_2O system) is taken into account by the general formula $M_{3m-3}T_{2m}O_{5m}(OH)_{4m-6}$ (Kunze 1961) where M and T are the octahedral (Mg^{2+}, Fe^{2+}, Ni^{2+}, Al^{3+}) and tetrahedral (Si^{4+}, Al^{3+}, Fe^{3+}) cationic sites, respectively, and m is the wavelength, i.e. the number of tetrahedra in a single chain along the a-axis. For natural antigorite, m = ⟦13;24⟧, which corresponds to ≈12.5 > C_{H2O} > ≈12 wt.% (Mellini et al., 1987). In other words, each polysomatic reaction (reduction of m with increasing T or decreasing P; Wunder et al. 2001) is a minor dehydration reaction.

Antigorite stability is known to depend on H_2O saturation (e.g. Perrillat et al. 2005; Hilairet et al. 2006). Perrillat et al. (2005) showed that a "talc-like" phase (5-13 wt.% H_2O) forms along with olivine at H_2O-unsaturated conditions, whereas antigorite remains stable

under H_2O saturation. The stability limit gradually shifts toward higher temperatures with increasing H_2O activity, with a maximum at the point of saturation (Perrillat et al. 2005). In addition, polysomatism is expected to release up to 4% of the H_2O content of antigorite (Wunder et al. 2001). The progressive H_2O loss stabilizes antigorite and is easily accommodated by further hydration reactions, which enhances serpentinization between the planes (Fig. 2) and forms other hydrous phases that are stable at high P-T conditions.

A mineral is metastable when it persists for an unbounded time outside of its stability field. The kinetics of a metamorphic reaction depends on the presence of a fluid phase, which promotes the mobility of atoms within a rock volume (e.g. Rubie 1990). Thus, the absence of fluid favors metastability. But for dehydration reactions, this kinetic effect is in competition with H_2O saturation. Indeed, H_2O stabilizes antigorite (Perrillat et al. 2005). Apparent "metastability" in transforming serpentinites at subduction conditions could actually be due to fluid circulations within serpentinized faults, allowing ions mobility between different regions of the serpentinized zone. Fluid percolation and repeated circulation events may allow some reaction products to migrate, as a supercritical fluid, up to the subduction channel. In other words, the uncertainty over local variations of mantle composition and connectivity of potential fluid pathways may be mistaken for "metastability". The latter may also refer to the difference in the stability limit in the P-T diagram between nominally pure phases and natural minerals with variable compositions (Ferrand 2019).

Stability limits and dehydration processes differ between serpentine varieties (Fig. 1). At atmospheric pressure, lizardite undergoes dehydroxylation between 550 and 625 °C (Trittschack and Grobéty 2013; Zhou et al. 2017), with a minimum activation energy of ≈220 $kJ \cdot mol^{-1}$. Chrysotile exhibits a progressive dehydration between 500 and 650 °C, where the dehydroxylation temperature depends on the nanotube diameter and is higher in the innermost layers compared to the less curved outer parts of the chrysotile fibres. Its activation energies range from 240 to 300 $kJ \cdot mol^{-1}$. For antigorite (m = 17), Liu et al. (2019) show that its dehydroxylation occurs over a wide temperature range, from ≈450 to ≈775°C, followed by a sharp breakdown step with a higher activation energy (≈300 $kJ \cdot mol^{-1}$). At high pressures, these values are expected to change, but the two-step mechanism should remain.

Under unsaturated conditions, talc-like phases form during the dehydration of antigorite (Perrillat et al. 2005), chrysotile (Trittschack et al. 2014) and lizardite (Gualtieri et al. 2012). The progressive fragmentation of silicate sheets enables a transition from directional to

3D mobility of H_2O through the structure of dehydrated serpentine minerals. Eventually, talc-like phases dehydroxylate during the last stage of chrysotile dehydration (Trittschack and Grobéty 2013), similar to that observed in the high-P experiments on antigorite (Perrillat et al. 2005).

The structure of antigorite contains connected nanopores enabling water flow (Tutolo et al. 2016; Schwarzenbach 2016), which helps deep mantle hydration near oceanic ridges (e.g. Dunn et al. 2018) or at trenches (Cai et al. 2018; Shillington 2018). These pathways may also facilitate H_2O redistribution within the subducting slab. Antigorite-rich rocks may, depending on antigorite connectivity, drain dehydration fluids from the lower plane through the interior of the double-seismic zone (Fig. 2).

Dehydrating antigorite forms anastomozed channels within serpentinites (Plümper et al. 2017), which consist of a mixture of olivine, talc-like and disordered serpentine. It is unclear whether the permeability of dehydrating antigorite would be higher or lower than the permeability of original antigorite itself. Thus, additional work is needed to understand how the sudden dehydration documented by Liu et al. (2019) could trigger or inhibit further dehydration.

Dehydration fluids transiently exist along the lower plane, as recently revealed by the high V_P/V_S ratio beneath northern Chile (Bloch et al. 2018). Supercritical H_2O rapidly diffuses as defects within olivine (Bai and Kohlstedt 1992), which may explain why the dehydration fluids are only seen near the lower plane. The sudden dehydration would promote the production of such abnormally deep fluid H_2O.

The study of Liu et al. (2019) confirms that antigorite dehydration is fast enough to trigger brittle failure under subduction conditions (Perrillat et al. 2005; Chollet et al. 2011; Ferrand et al. 2017; Inoue et al. 2009). This is also the case for other hydrous phases, e.g. talc and 10-Å phase (Chollet et al. 2009). Dehydration reactions of single phases are typically fast. Such transformations produce extremely fine mineral aggregates, are prone to initiate strain localization by thermal runaway (e.g. Thielmann 2017), and promote critical stress transfers triggering mechanical instabilities (Ferrand 2017). The stability limit of antigorite depends on chemistry, fluid mobility and saturation conditions. Finally, as antigorite is not “metastable” under subduction conditions, if some of the seismicity does not correlate with antigorite dehydration, the decomposition of other hydrous or carbonated phases needs to be considered (Ferrand 2019).

This is a preprint, the final version is subject to change, of the American Mineralogist (MSA)
Cite as Authors (Year) Title. American Mineralogist, in press.
DOI: https://doi.org/10.2138/am-2019-6957

Through this experimental work, Liu et al. (2019) also recall the relevance of 1-atm experiments and their non-isothermal TGA provides insight as to how an antigorite crystal destabilizes, answering a question that high-pressure experiments could not fully address.

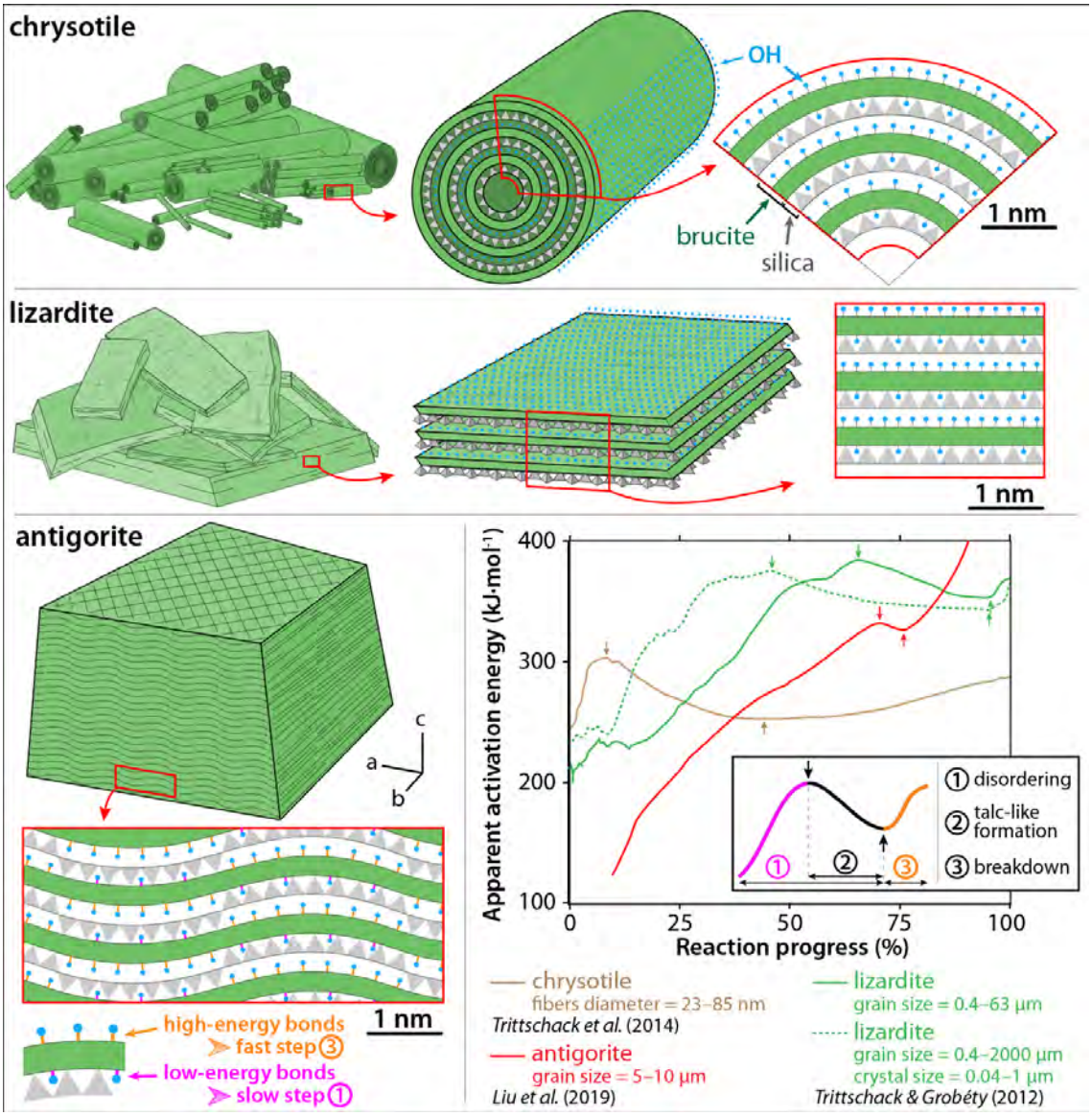

Figure 1. The dehydroxylation mechanism of serpentine minerals. Chrysotile, lizardite and antigorite have different structures, which control their stability limits and dehydration kinetics. Arrows indicate the expected limits of existence of talc-like on the activation energy curves.

This is a preprint, the final version is subject to change, of the American Mineralogist (MSA)
Cite as Authors (Year) Title. American Mineralogist, in press.
DOI: https://doi.org/10.2138/am-2019-6957

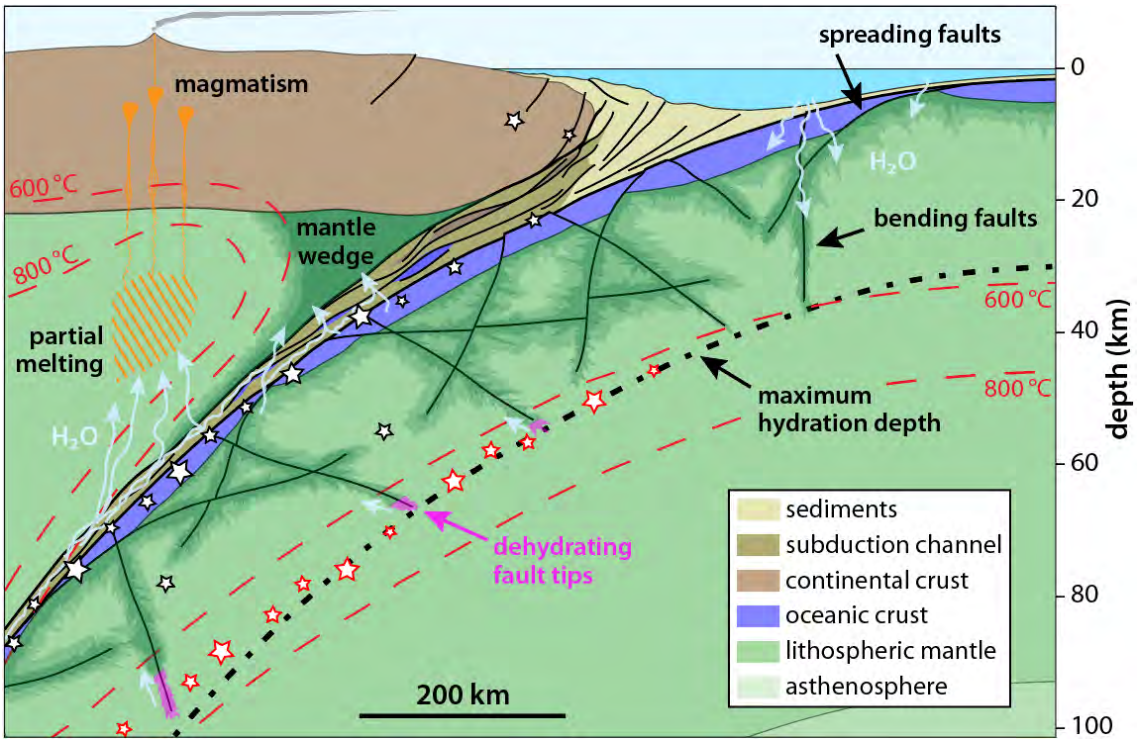

Figure 2. Antigorite dehydration and double seismic zone. Stars represent earthquakes, red for the lower Wadati-Benioff plane and white for other earthquakes. Dark green corresponds to high serpentinization near faults and in the mantle wedge.

References

1. Abers, G.A., Nakajima, J., van Keken, P.E., Kita, S., and Hacker, B.R. (2013) Thermal-petrological controls on the location of earthquakes within subducting plates. Earth and Planetary Science Letters, 369, 178-187.
2. Bai, Q., and Kohlstedt, D. L. (1992) Substantial hydrogen solubility in olivine and implications for water storage in the mantle. Nature, 357(6380), 672.
3. Bloch, W., John, T., Kummerow, J., Salazar, P., Krüger, O. S., and Shapiro, S. A. (2018) Watching Dehydration: Seismic Indication for Transient Fluid Pathways in the Oceanic Mantle of the Subducting Nazca Slab. Geochemistry, Geophysics, Geosystems, 19(9), 3189-3207.
4. Cai, C., Wiens, D.A., Shen, W., and Eimer , M. (2018) Water input into the Mariana subduction zone estimated from ocean-bottom seismic data. Nature, 563, 389-392.
5. Chernak, L., and Hirth G. (2010) Deformation of antigorite serpentinite at high temperature and pressure. Earth and Planetary Science Letters, 296 (1-2), 23-33.
6. Chernak, L., and Hirth G. (2011) Syndeformational antigorite dehydration produces stable fault slip. Geology, 39 (9), 847-850.
7. Dunn, R.A., Arai, R., Eason, D.E., Canales, J.P., and Sohn, R.A. (2017) Three-Dimensional Seismic Structure of the Mid-Atlantic Ridge: An Investigation of Tectonic, Magmatic, and Hydrothermal Processes in the Rainbow Area. Journal of Geophysical Research: Solid Earth, 122, (12), 9580-9602.
8. Ferrand, T.P., Hilairet, N., Incel, S., Deldicque, D., Labrousse, L., Gasc, J., ..., and Schubnel, A. (2017) Dehydration-driven stress transfer triggers intermediate-depth earthquakes. Nature Communications, 8.

9. Ferrand, T.P. (2019) Seismicity and mineral destabilizations in the subducting mantle up to 6 GPa, 200 km depth. Lithos.
10. Gasc, J., Schubnel, A., Brunet, F., Guillon, S., Mueller, H., and Lathe, C. (2011) Simultaneous acoustic emissions monitoring and synchrotron X-ray diffraction at high pressure and temperature: Calibration and application to serpentinite dehydration. Physics of Earth and Planetary Interiors, 189, 121-133.
11. Gualtieri, A. F., Giacobbe, C.,, and Viti, C. (2012) The dehydroxylation of serpentine group minerals. American Mineralogist, 97(4), 666-680.
12. Kita, S., and Ferrand, T.P. (2018) Physical mechanisms of oceanic mantle earthquakes: Comparison of natural and experimental events. Scientific Reports, 8, 17049.
13. Hacker, B.R., Peacock, S.M., and Abers, G.A. (2003) Subduction factory: 2. Intermediate-depth earthquakes in subducting slabs are linked to metamorphic dehydration reactions. Journal of Geophysical Research: Solid Earth, 108.
14. Inoue, T., Yoshimi, I., Yamada, A., and Kikegawa, T. (2009) Time-resolved X-ray diffraction analysis of the experimental dehydration of serpentine at high pressure. Journal of Mineralogical and Petrological Sciences, 104(2), 105-109.
15. Liu, T., Wang, D., Shen, K., Liu, C., and Yi, L. (2019) Kinetics of antigorite dehydration, American Mineralogist.
16. Chollet, M., Daniel, I., Koga, K. T., Petitgirard, S., and Morard, G. (2009) Dehydration kinetics of talc and 10 Å phase: Consequences for subduction zone seismicity. Earth and Planetary Science Letters, 284(1-2), 57-64.
17. Chollet, M., Daniel, I., Koga, K. T., Morard, G., and van de Moortèle, B. (2011) Kinetics and mechanism of antigorite dehydration: Implications for subduction zone seismicity. Journal of Geophysical Research: Solid Earth, 116, 1-9.
18. Kunze, G. (1961) Antigorit. Strukturtheoretische Grundlagen und ihre praktische Bedeutung für die weitere Serpentin-Forschung. Fortschritte in Mineralogie, 9, 206-324.
19. Mellini, M., Trommsdorff, V., Compagnoni, R. (1987) Antigorite polysomatism: behaviour during progressive metamorphism. Contributions to Mineralogy and Petrology, 97, 147-155.
20. Perrillat, J.-P., Daniel, I., Koga, K.T., Reynard, B., Cardon, H., and Crichton W. A. (2005) Kinetics of antigorite dehydration; a real-time X-ray diffraction study. Earth and Planetary Science Letters, 236, 899-913.
21. Hilairet, N., Daniel, I., and Reynard, B. (2006) Equation of state of antigorite, stability field of serpentines, and seismicity in subduction zones. Geophysical Research Letters, 33(2).
22. Okazaki, K., and Hirth, G. 2016. Dehydration of lawsonite could directly trigger earthquakes in subducting oceanic crust. Nature, 530(7588), 81.
23. Plümper, O., John, T., Podladchikov, Y. Y., Vrijmoed, J. C., and Scambelluri, M. (2017) Fluid escape from subduction zones controlled by channel-forming reactive porosity. Nature Geoscience, 10(2), 150.
24. Peacock, S. (2001) Are the lower planes of double seismic zones caused by serpentine dehydration in subducting oceanic mantle? Geology, 29(4), 299-302.
25. Rubie, D. C. (1990) Role of kinetics in the formation and preservation of eclogites. Eclogite facies rocks, 111-140.
26. Scambelluri, M., Pennacchioni, G., Gilio, M., Bestmann, M., Plümper, O., and Nestola, F. (2017) Fossil intermediate-depth earthquakes in subducting slabs linked to differential stress release. Nature Geoscience, 10, 960-96.
27. Schwarzenbach, E. M. (2016) RESEARCH FOCUS: Serpentinization and the formation of fluid pathways. Geology, 44(2), 175-176.
28. Shillington, D. J. (2018) Water takes a deep dive into the Mariana Trench. Nature, 563(7731), 335-336.
29. Thielmann, M. (2017) Grain size assisted thermal runaway as a nucleation mechanism for continental mantle earthquakes: Impact of complex rheologies. Tectonophysics, 746, 611-623.

30. Trittschack, R., and Grobéty, B. (2012) Dehydroxylation kinetics of lizardite. European Journal of Mineralogy, 24(1), 47-57.
31. Trittschack, R., and Grobéty, B. (2013) The dehydroxylation of chrysotile: A combined in situ micro-Raman and micro-FTIR study. American mineralogist, 98(7), 1133-1145.
32. Trittschack, R., Grobéty, B., and Brodard, P. (2014) Kinetics of the chrysotile and brucite dehydroxylation reaction: a combined non-isothermal/isothermal thermogravimetric analysis and high-temperature X-ray powder diffraction study. Physics and Chemistry of Minerals, 41(3), 197-214.
33. Tutolo, B.M., Mildner, D.F.R., Gagnon, C.V.L., Saar, M.O., and Seyfried, W.E. (2016) Nanoscale constraints on porosity generation and fluid flow during serpentinization: Geology, 44, 103-106.
34. Wang, D., Yi, L., Huang, B., and Liu, C. (2015) High-temperature dehydration of talc: a kinetics study using in situ X-ray powder diffraction. Phase Transitions, 88(6), 560-566.
35. Wunder, B., and Schreyer, W. (1997) Antigorite: High pressure stability in the system MgO-SiO_2-H_2O (MSH). Lithos, 41, 213-227.
36. Wunder, B., Wirth, R., and Gottschalk, M. (2001) Antigorite pressure and temperature dependence of polysomatism and water content. European Journal of Mineralogy, 13(3), 485-496.
37. Zhou, S., Wei, Y., Li, B., Ma, B., Wang, C., and Wang, H. (2017). Kinetics study on the dehydroxylation and phase transformation of $Mg_3Si_2O_5(OH)_4$. Journal of Alloys and Compounds, 713, 180-186.