

## Review

# Review of secondary phases formed under natural alkaline conditions at low temperatures and implications for cement–bentonite interactions in radioactive waste repositories

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### Abstract

The alteration of bentonite under alkaline conditions and the subsequent changes in properties such as permeability and self-sealing ability should be evaluated for the performance assessment of radioactive waste repositories. As the period of evaluation for alterations is extremely long, natural analog (NA) studies that can observe long-term phenomena similar to the system of radioactive waste repositories have significant advantages. However, locations that can be set up as NA study sites with significant similarity are limited and should be pursued by localizing analog systems. This literature review summarized studies reporting secondary phases formed at low temperatures (<100°C) under a broader range of natural sites which are chemically similar to the alkaline conditions expected at bentonite in radioactive waste repositories, including near pyrometamorphic rocks, near ophiolites, and in alkaline saline lakes. This review provides insights into the species, formation conditions, and stability of secondary phases that could be formed during cement–bentonite interactions and the timescale for mineralogical transitions from a metastable to a stable phase. The findings could be useful for selecting secondary phases to be considered in reactive transport modeling for predicting cement–bentonite interactions in radioactive waste repositories.

**Keywords:** alkaline saline lake; cement–bentonite interaction; natural analog; ophiolite; pyrometamorphic rock; secondary phase

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### Introduction

#### Background

Bentonite will be used as an engineered barrier in radioactive waste repositories which are designed such that the maximum temperature does not exceed 100°C (NUMO, 2021). One of the main purposes for using bentonite in radioactive waste repositories is to retard radionuclide migration; the properties of bentonite which allow this are its low permeability and self-sealing ability (Sellin and Leupin, 2013; NUMO, 2021). The low permeability and self-sealing ability can be attributed to the amount and properties of montmorillonite, the main constituent of bentonite.

Cementitious materials are often installed around bentonite as engineered barriers or peripheral components (Tyupina *et al.*, 2023 and references therein), and they produce alkaline leachate with a pH range of 10–13.5 (Andersson *et al.*, 1989; García Calvo *et al.*, 2010). As montmorillonite is known to dissolve under alkaline

conditions (Cama *et al.*, 2000; Yokoyama *et al.*, 2005), there is a concern that the alkaline alteration of bentonite induced by leachate from cementitious materials may increase permeability. In reality, however, the alteration of bentonite is a complex reaction that includes not only the dissolution of montmorillonite but also other reactions, including precipitation of secondary phases. Furthermore, the formation of secondary phases has a significant impact on permeability changes of bentonite.

The evaluation of alkaline alteration of bentonite is necessary for the performance assessment of radioactive waste repositories. However, it is impossible to conduct experiments in which bentonite and cementitious materials interact over thousands of years. Therefore, the long-term alteration of bentonite must be estimated using reactive transport (RT) modeling, which considers the dissolution of primary minerals in bentonite and the precipitation of secondary phases. Of these, data have been reported on mineral dissolution, including its kinetics (Bandstra *et al.*, 2008; Cama and Ganor, 2015), and the kinetics of mineral dissolution appears to be ready to be implemented in RT modeling. Conversely, with regard to the precipitation of secondary phases, the chemical environment assumed in radioactive waste repositories is spatiotemporally complex, and the potential secondary phase species are established in various manners accordingly. Furthermore, knowledge of the subsequent

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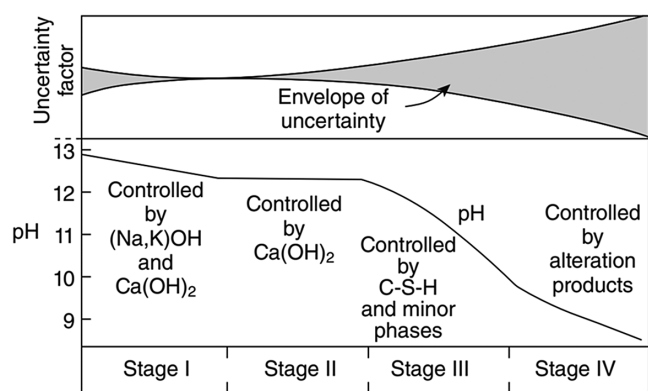
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mineralogical transition of the secondary phases formed in the RT modeling is lacking, which leads to uncertainty in the modeling results; therefore, it is important to examine how to select secondary phases and parameters related to these secondary phases in RT modeling.

To understand the alkaline alterations of bentonite, including the formation of secondary phases, several laboratory and *in situ* experiments have been conducted (Sánchez *et al.*, 2006; Fernández *et al.*, 2016; Fernández *et al.*, 2017; Yokoyama *et al.*, 2021). However, there is a significant disparity in the timescales of reactions in those experiments and actual radioactive waste repositories. To understand the reaction of secondary phases formed by long-term geochemical reactions and examine how to select secondary phases to be considered in the RT modeling, it is necessary to observe geochemical reactions under alkaline conditions in nature along with laboratory and *in situ* experiments. In this review, the reactions forming the secondary phases in diverse natural alkaline environments at low temperatures (<100°C) were reviewed to understand species, formation conditions, and mineralogical transition of secondary phases that have the potential to form during cement–bentonite interactions in radioactive waste repositories. In the following sections, the alkaline conditions derived from cementitious materials, the impact of secondary phases on the permeability change of bentonite, and the advantages of investigations on natural geochemical reactions are comprehensively discussed.

#### Alkaline conditions derived from cementitious materials

Alkaline leachate is generated by the interaction between cementitious materials and groundwater in radioactive waste repositories. The composition of alkaline leachate varies with the stage of cement degradation. For example, the overall evolution of the chemical composition of leachate from ordinary Portland cement (OPC) can be divided into four stages, as follows (Fig. 1): (1) Stage I:



**Figure 1.** Evolution of ordinary Portland cement leachate and associated uncertainties (Glasser, 2011).

**Table 1.** Examples of chemical compositions of cement leachates

Stage	pH*	Na*	K*	Ca*	Al*	Si*	S*
I	13.2	$1.15 \times 10^{-1}$	$1.00 \times 10^{-1}$	$2.52 \times 10^{-3}$	$3.04 \times 10^{-5}$	$1.22 \times 10^{-4}$	$1.97 \times 10^{-3}$
II	12.5	$9.84 \times 10^{-3}$	$6.44 \times 10^{-3}$	$9.21 \times 10^{-3}$	$5.00 \times 10^{-5}$	$2.79 \times 10^{-6}$	$7.71 \times 10^{-5}$
III	11.3	$2.96 \times 10^{-3}$	—	$3.62 \times 10^{-4}$	$7.00 \times 10^{-5}$	$1.53 \times 10^{-4}$	$4.80 \times 10^{-4}$

\*Data sourced from Savage *et al.* (2002). The concentrations are expressed in mol dm<sup>-3</sup>.

the leachate is dominated by highly soluble alkali hydroxides (Berner, 1992; Glasser, 2011), which has a pH of ~13 and is rich in K and Na ions (García Calvo *et al.*, 2010); (2) Stage II: the leachate is dominated by Ca(OH)<sub>2</sub>, and the pH is buffered at ~12.5 (Berner, 1992; Glasser, 2011); (3) Stage III: the leachate is determined by the C–S–H gel, depending on the Ca:Si ratio of the gel; the pH decreases continuously to 11 (Berner, 1992; Glasser, 2011); and (4) Stage IV: the leachate is controlled by alteration products (Glasser, 2011). Estimates in given conditions predicted that Stage I can last ~10,000 y and Stage II can last from 10,000 to 200,000 y (Sun *et al.*, 2022 and references therein), although the leachate evolution period can be affected by the chemical composition of the groundwater (Atkinson *et al.*, 1985; Berner, 1992). In Savage *et al.* (2002), the chemical compositions of the simulated leachates in Stages I–III were set out as illustrated in Table 1.

Furthermore, the composition of alkaline leachate varies with the type of cementitious material. For example, the chemical composition of the alkaline leachate changes when supplementary cementitious materials, such as silica fume or fly ash, are mixed with OPC (García Calvo *et al.*, 2010; Vollpracht *et al.*, 2016). García Calvo *et al.* (2010) reported that low-alkali cement, in which silica fume and fly ash were added to OPC, produced leachates containing smaller amounts of K and Na ions and larger amounts of SO<sub>4</sub> ions. Additionally, an increase in supplementary cementitious materials decreases pH (Vollpracht *et al.*, 2016), and therefore, there is growing interest in using low-alkali cement with an initial pH of 9–11 as an alternative to OPC due to concerns about bentonite alteration under the highly alkaline conditions generated by OPC degradation (Milodowski *et al.*, 2016).

#### Impact of secondary phases on permeability change of bentonite

During cement–bentonite interactions, the formation of secondary phases can promote or inhibit the permeability increase of bentonite. For example, the formation of secondary phases can contribute to a decrease in the porosity of bentonite, thereby decreasing its permeability (Yokoyama *et al.*, 2011). Conversely, in some cases, the formation of Si-containing secondary phases decreases the Si concentration in the pore solution. As a decrease in the Si concentration in a pore solution enhances the dissolution of montmorillonite due to the effect of the degree of undersaturation (Cama *et al.*, 2000; Cappelli *et al.*, 2018), this may increase the permeability. Furthermore, the precipitation of secondary phases changes the pH of the pore solution, which affects the dissolution kinetics of the montmorillonite (Rozalén *et al.*, 2008). Notably, the effect of secondary-phase precipitation on the pore solution chemistry and porosity depends on the species of the secondary phases; therefore, the species of secondary phases formed during

bentonite alteration could impact the permeability change of bentonite.

Additionally, metastable phases, which are not thermodynamically stable, can be formed during the alteration process as the dissolution of the primary minerals and precipitation of secondary phases are governed by kinetics. For example, in the alkaline alteration of tuffaceous sedimentary rocks, the rate of dissolution of the glass is so quick that it is supersaturated for the metastable phase. This results in the precipitation of metastable phases with a fast precipitation rate, followed by a transition to thermodynamically more stable minerals with a slower precipitation rate over time (Dibble and Tiller, 1981). A similar mineralogical transition is expected in the alkaline alteration of bentonite (Savage *et al.*, 2007). In other words, during the long-term alteration of bentonite under alkaline conditions, not only is a mineral transition owing to changes in the chemical environment caused by external factors (e.g. changes in the solution composition of pore water from cementitious materials) but also a transition from a metastable phase to stable minerals even in a stable chemical environment is expected. The mineralogical transitions after the precipitation of secondary phases may further alter permeability. This indicates that the mineralogical transitions of the secondary phases within the evaluation period may need to be considered when evaluating the long-term permeability changes in bentonite.

#### Advantages of investigations on natural geochemical reactions

As mentioned previously, the evaluation period of bentonite alterations in radioactive waste repositories is extremely long, and the chemical conditions to be assumed are diverse. Laboratory experiments, *in situ* experiments, and natural analog (NA) studies differ in the amount of data produced, diversity of the chemical conditions that can be considered, and observation period of the phenomena (Shimbashi *et al.*, 2022a; Fig. 2). To understand bentonite alteration under diverse chemical conditions over long periods of time, it is important to combine knowledge from these three research methods.

Natural analog studies involve the observation of systems in nature that are analogs of the phenomena concerned (i.e. conditions in radioactive waste repositories). The advantage of this approach is that phenomena can be observed over a long period (Fig. 2); however, relatively few locations exist that can be set up as study sites with significant similarity to the system of radioactive waste repositories. Indeed, previous NA studies at

sites where bentonite has interacted directly with alkaline fluids in nature are limited to two case studies, reported by Fujii *et al.* (2014) and Milodowski *et al.* (2016). Therefore, it is important to proceed with NA studies with the stance that localized analog systems are acceptable as long as the target to be reflected in the radioactive waste repository system is clear (Yoshida *et al.*, 2010). This review compiles geochemical reactions, including the precipitation reactions of secondary phases at several alkaline environments in nature, that are chemically similar to the alkaline leachate of cementitious materials. Although there have been previous reviews compiling natural geochemical reactions to understand cement–bentonite or cement–clay rock interactions (Gaucher and Blanc, 2006; Savage *et al.*, 2007; Savage, 2011), the present review is unique in that it organizes geochemical reactions under a broader range of natural sites as described in the next section and includes the latest findings since previous reviews. Furthermore, this review provides implications for the species and mineralogical transitions of secondary phases resulting from long-term bentonite–cement interactions, taking into account the spatial distribution of bentonite in radioactive waste repositories and changes in the chemistry of alkaline leachate from cementitious materials over time. This will play an important role in selecting secondary phases to be considered in the RT modeling of bentonite–cement interactions and parameters related to these secondary phases.

#### Natural sites covered in this literature review

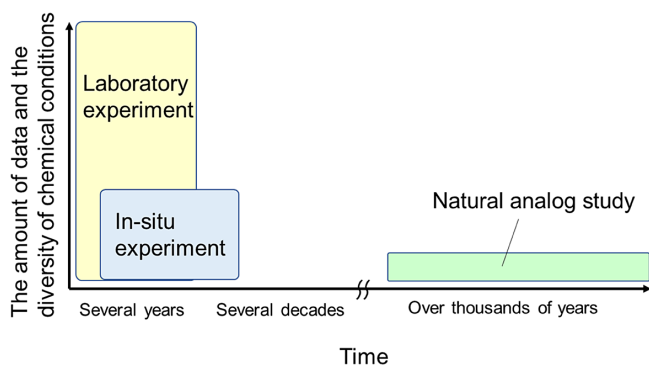
In this review, three types of natural sites that produce alkaline fluid at low temperatures were compiled, near pyrometamorphic rocks, ophiolites, and alkaline saline lakes. As noted above, this is unique because previous reviews compiled natural geochemical reactions near pyrometamorphic rocks (Gaucher and Blanc, 2006; Savage *et al.*, 2007; Savage, 2011) and in alkaline saline lakes (Savage *et al.*, 2007; Savage, 2011) but not for ophiolite.

Here, the mechanisms of formation of natural alkaline fluids at the three types of sites and the chemical compositions of the alkaline fluid produced at each site type are described. Furthermore, the analogy of the chemical environments at each site type for cement–bentonite interactions in radioactive waste repositories is discussed.

#### Formation sites and mechanisms of natural alkaline fluids

Alkaline fluids with a pH of  $\sim 12.5$  were recognized near pyrometamorphic rocks in the western and eastern springs in the Maqarin area of Jordan (Khoury *et al.*, 1992). In Maqarin, natural cements are produced by the pyrometamorphism of marls, and alkaline fluids are produced by interactions between these natural cements and groundwater (Kamei *et al.*, 2010; Pitty and Alexander, 2011).

The formation of alkaline fluids in ophiolite aquifers has been recognized worldwide (Barnes and O'Neil, 1969; Barnes and O'Neil, 1978). The alkaline fluids found near ophiolites can be divided into two types: Ca-OH and Mg-HCO<sub>3</sub> types (Barnes and O'Neil, 1969). Several Ca-OH types have a pH of  $>11$  (Bruni *et al.*, 2002; Giampouras *et al.*, 2020), whereas the Mg-HCO<sub>3</sub> type has a pH of  $\sim 9$  (Okland *et al.*, 2012; Giampouras *et al.*, 2020). The production of alkaline fluids of intermediate quality by mixing these two types of alkaline fluids has also been reported (mix type; Giampouras *et al.*, 2020). These types of alkaline fluids are



**Figure 2.** Conceptual diagram of the reaction times and diversity of data and chemical conditions covered by each research method. Adapted from Shimbashi *et al.* (2022a).

considered to be of meteoric origin, and previous studies suggested water–rock interaction mechanisms that could produce them (Bruni *et al.*, 2002). Specifically, the interaction of serpentinite with immature Mg-rich  $\text{SO}_4\text{-Cl}$  water, an early product in the evolution of rainwater, produces Mg- $\text{HCO}_3$ -type alkaline fluids under open-system conditions for atmospheric  $\text{CO}_2$ . Under closed-system conditions with respect to atmospheric  $\text{CO}_2$ , these Mg- $\text{HCO}_3$ -type alkaline fluids evolve into Ca-OH-type alkaline fluids via interactions with serpentinite (Bruni *et al.*, 2002). Here, the question arose as to why Ca-OH-type alkaline fluids are rich in Ca and low in Mg despite the fluids interacting with MgO-rich and CaO-poor rocks, such as serpentinites. The former question can be answered by the role of calcite precipitation in depleting the aqueous solution of C species, allowing the increase in Ca supplied by the dissolution of serpentinite despite its relatively low CaO content (Bruni *et al.*, 2002). Regarding the latter question, precipitation of brucite and serpentine depletes Mg in the fluids (Marques *et al.*, 2008). With these water–rock interactions, the pH of the fluids increased, and fluids evolved into Ca-OH-type.

The chemical composition of alkaline saline lakes is attributed to the evaporation of lake water (Darragi and Tardy, 1987; Barbiéro *et al.*, 2002). For example, in the case of an alkaline saline lake in the Pantanal Wetland, Brazil, it was suggested that some ions, such as  $\text{Na}^+$ , and carbonate alkalinity increase linearly during evaporation, whereas  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are consumed by precipitation. The pH value increased from  $\sim 7$  to 10 during this process (Barbiéro *et al.*, 2002).

#### Chemical compositions of natural alkaline fluids

To compare the chemical compositions of the alkaline fluids at each site type, a Piper diagram and scatter plots are shown in Fig. 3 and Fig. 4, respectively. The plots are based on the following reported chemical compositions: near pyrometamorphic rocks (Khoury *et al.*, 1992), near ophiolites (Bruni *et al.*, 2002; Giampouras *et al.*, 2020; Okland *et al.*, 2012), and near alkaline saline lakes (Taylor and

Surdam, 1981). Cited values of chemical compositions of the alkaline fluids to create the diagrams are provided in Appendix A of the Supplementary material.

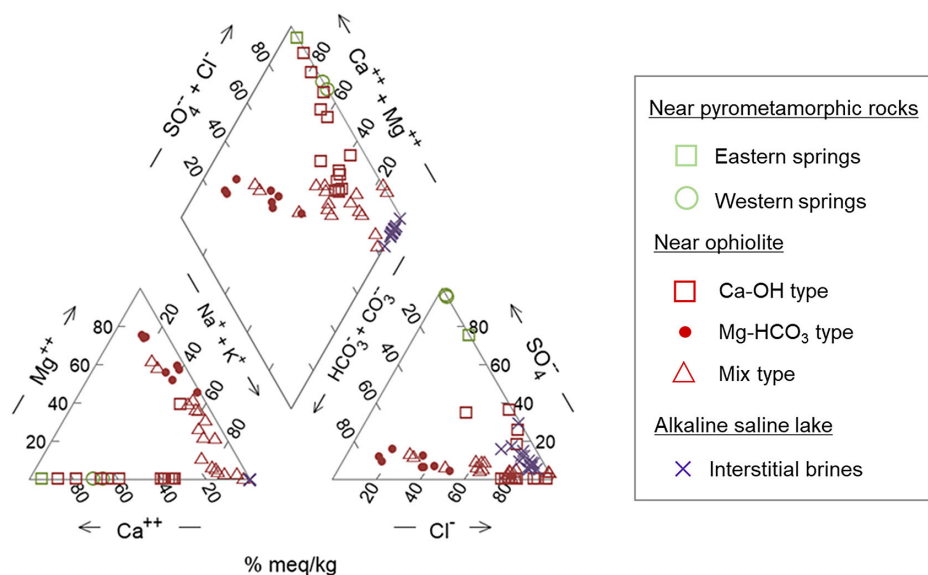
The alkaline fluids with a high pH of  $>11$  are produced near pyrometamorphic rocks and near ophiolites (Ca-OH-type). A common feature of these alkaline fluids is that they are rich in  $\text{Ca}^{2+}$  ions, with a certain amount of  $\text{Na}^+$  or  $\text{K}^+$  ions also observed, but low concentrations of  $\text{Mg}^{2+}$  ions (Figs 3 and 4). Moreover, the alkaline fluids near pyrometamorphic rocks are rich in  $\text{SO}_4^{2-}$  ions, while the Ca-OH-type alkaline fluids near ophiolites are rich in  $\text{Cl}^-$  ions. Both of these alkaline fluids were found to contain low concentrations of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions (Fig. 3).

The Mg- $\text{HCO}_3$ -type alkaline fluids near ophiolite and alkaline fluids in alkaline saline lakes have a lower pH. The Mg- $\text{HCO}_3$ -type alkaline fluids were rich in  $\text{Mg}^{2+}$  ions and  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  ions, compared with the alkaline fluids described above. The alkaline fluids in alkaline saline lakes are characterized by a lack of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions and a high concentration of  $\text{Na}^+$  or  $\text{K}^+$  ions (Figs 3 and 4).

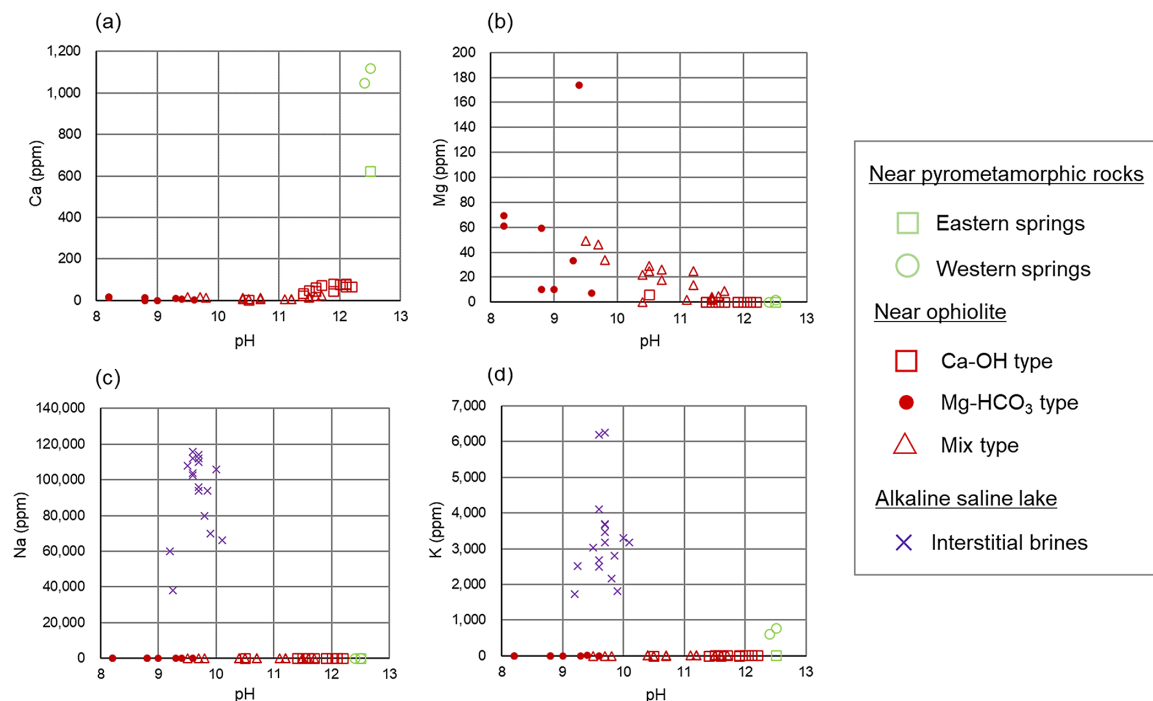
The chemistry of mix-type alkaline fluids near ophiolite exhibited characteristics intermediate between the Ca-OH-type and Mg- $\text{HCO}_3$ -type (Fig. 3).

#### Analogs to radioactive waste repositories

The alkaline environment expected in a radioactive waste repository varies spatiotemporally. In particular, the chemical composition of the alkaline leachate from cementitious materials is expected to change over time (Fig. 1). The spatial distribution of pH at bentonite is expected to differ owing to the decrease in pH of alkaline leachate caused by migrating and potentially chemically reacting with the bentonite (Savage, 2011). Furthermore, the chemical composition of the groundwater and the design of radioactive waste repositories also affect bentonite–cement interactions. Different designs for radioactive waste repositories depending on waste type have been proposed in various countries. For example, in one option for a



**Figure 3.** Piper diagram showing the chemical compositions of the alkaline fluids produced at each site. Values of chemical compositions of the alkaline fluids to create the Piper diagram are provided in Appendix A of the Supplementary material.



**Figure 4.** Dissolved ion concentrations at different pH values of the alkaline fluids: (a) Ca ion; (b) Mg ion; (c) Na ion; (d) K ion. Values of chemical compositions of the alkaline fluids to create the scatter plots are provided in Appendix A of the Supplementary material.

spent fuel repository in Switzerland (Sellin and Leupin, 2013) or in an option for TRU waste in Japan (Ichikawa and Hamamoto, 2021), the tunnel would be supported by shotcrete, and bentonite would be placed inside the tunnel. On the other hand, for long-lived low- and intermediate-level waste (LL-LILW) in Sweden, bentonite materials would be placed around concrete (Elfving *et al.*, 2013). For high-level radioactive waste in Japan, bentonite would be placed in a deposition hole below the tunnel supported by shotcrete (Ichikawa and Hamamoto, 2021). Fluids, after interaction between shotcrete and groundwater, may leach to bentonite in the case of spent fuel in Switzerland and TRU waste in Japan, whereas first groundwater and then alkaline leachates from concrete may leach to bentonite in the case of LL-LILW in Sweden and high-level radioactive waste in Japan. In other words, different fluid chemistries leaching to bentonite make different chemical conditions. Figure 5 shows a conceptual diagram of spatiotemporal bentonite–cement interactions depending on different chemical conditions, Mg-rich or not. As noted earlier, there is more than one design of radioactive waste repository. How the chemistry of alkaline fluids near pyrometamorphic rocks, ophiolites, and alkaline saline lakes is analogous with bentonite interacting with cementitious materials is illustrated in Figure 5.

Based on the chemical compositions of alkaline fluids near pyrometamorphic rocks and the Ca-OH-type alkaline fluids near ophiolites (Fig. 3), the chemical environment in which the secondary phases form at these sites would mainly be analogous to the alteration of bentonite close to cementitious materials with Stage II alkaline leachates (Fig. 5). As a certain amount of  $\text{Na}^+$  or  $\text{K}^+$  ions are also recognized in these alkaline fluids (Fig. 3), those alkaline fluids may also be analogous to Stage I alkaline leachates, possibly of a relatively late stage within Stage I. Indeed, the alkaline fluids near the pyrometamorphic rocks are considered analogous to

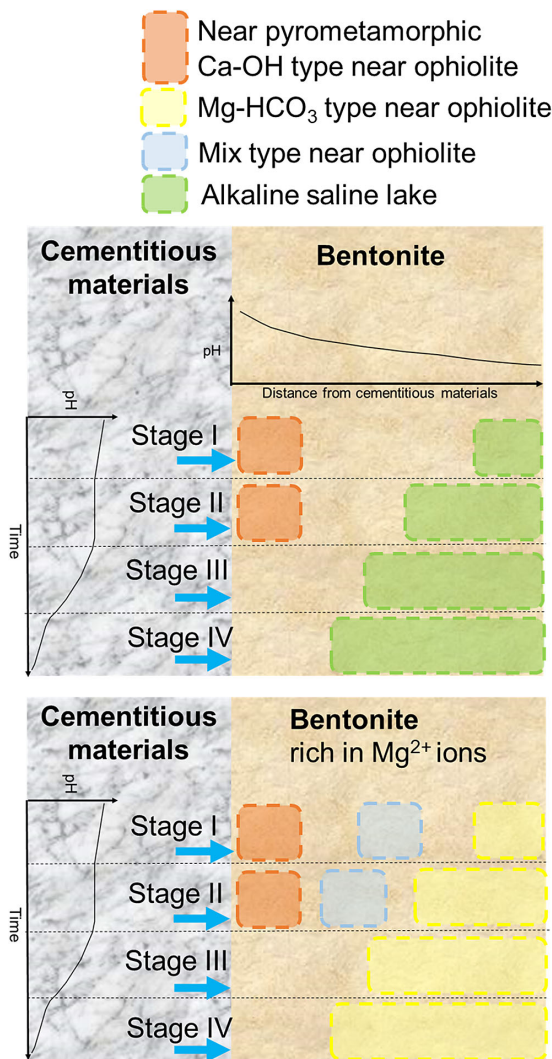
the alkaline leachates from cementitious materials (Pitty and Alexander, 2011). Moreover, Ca-OH-type alkaline fluids near ophiolites are considered analogous to alkaline leachates from low-pH cement (Fujii *et al.*, 2014; Milodowski *et al.*, 2016), or even from OPC (Fujii *et al.*, 2014).

Based on the chemical compositions of alkaline saline lakes (Fig. 3), the chemical environment in which the secondary phases form at these sites may be analogous to the alteration of bentonite that occurs under relatively low pH conditions farther from the interface between cementitious materials and bentonite (Fig. 5). Indeed, geochemical reactions in alkaline saline lakes are believed to be similar to those associated with alkaline leachates that progressively interact with rocks (Savage, 2011).

Similarly, the Mg- $\text{HCO}_3$ -type alkaline fluids near ophiolites may be analogous to the chemical environment in which secondary phases are formed by the alteration of bentonite farther from the cementitious materials and under Mg-rich conditions (Fig. 5), such as when seawater (dissolved at  $\sim 1200 \text{ mg L}^{-1}$  of  $\text{Mg}^{2+}$  in Kang *et al.* (2014)) leach to bentonite.

As the chemistry of mix-type alkaline fluids showed characteristics intermediate between the Ca-OH-type and the Mg- $\text{HCO}_3$ -type (Fig. 3), they may be analogous to the chemical environment at the intermediate part of the bentonite, where Ca-OH-type and Mg- $\text{HCO}_3$ -type each have similarities (Fig. 5).

In summary, the chemistry of alkaline fluids produced near pyrometamorphic rocks, ophiolites, and alkaline saline lakes is analogous to cement–bentonite interactions in radioactive waste repositories at different times and spaces (Fig. 5); thus, compiling previous literature describing secondary phases at these three types of sites will provide an understanding of potential secondary phases that may be formed during cement–bentonite interactions at various timescales and in various environments in radioactive waste repositories.



**Figure 5.** Conceptual diagram showing how the chemistry of alkaline fluids near pyrometamorphic rocks, ophiolites, and alkaline saline lakes are analogous with those of cement–bentonite interactions in radioactive waste repositories at various times and spaces.

### Secondary phases under natural alkaline conditions

The secondary phases reported to occur near pyrometamorphic rocks and with Ca-OH-type alkaline fluids in ophiolites (Table 2), with Mg-HCO<sub>3</sub>-type and mix-type alkaline fluids in ophiolites (Table 3), and in alkaline saline lakes (Table 4) are summarized below.

#### Near pyrometamorphic rocks

The site in the Maqarin area of Jordan has been studied extensively (Kamei *et al.*, 2010; Pitty and Alexander, 2011). The alkaline alteration of the host rocks in the western and eastern springs is similar, despite variations in their primary lithologies and mineralogy (Baker *et al.*, 2002). For example, Martin *et al.* (2016) collected samples from adits through which alkaline fluids flow in the eastern springs of the Maqarin area. Calcium–aluminum–silicate–hydrate (C–A–S–H) precipitated from the alkaline fluids in the veins and the adjacent biomicroite. When the solution evolved to a more S-rich solution, ettringite, and

thaumasite precipitated in C–A–S–H veins under Al-rich and Al-poor conditions, respectively (Martin *et al.*, 2016). It is worth noting that thaumasite formation is affected not only by molar SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, but also by temperature, with thaumasite formation being favored at temperatures of <8°C (Schmidt *et al.*, 2008). Zeolite (possibly chabazite) precipitated downstream in the low pH regions of the alkaline fluids. Among the precipitates, C–A–S–H gels are sensitive to carbonation, and the C–A–S–H gels decompose to form a mixture of Si- and Al-rich gels and calcite (Martin *et al.*, 2016).

#### Near ophiolites

##### Ca-OH type

Alkaline alteration of bentonite has been reported on Luzon Island in the Philippines (Fujii *et al.*, 2014). Fractures of pillow lava connected to bentonite. As chrysotile was recognized in the fractures, it is indicated that alkaline fluids produced in ophiolite may have leached into the bentonite using the fractures as flow paths. At the contact with the fractures filled with chrysotile, bentonite was altered to within 5 mm, and the altered layer was divided into two layers. In the layer on the fracture side, the formation of Ca-zeolite (clinoptilolite and heulandite), silica minerals, and K-feldspar was reported. In the adjacent layer, K-feldspar, pyrite, and nontronite were reported. In other outcrops, chrysotile and calcite were found within the fractures, and calcite was formed at the boundary between the fractures and bentonite.

The alkaline alteration of bentonite has also been reported in the Parsata area of Cyprus (Milodowski *et al.*, 2016). In the alteration zone, which is believed to have been altered by reactions with alkaline fluids, Fe-bearing palygorskite was formed over 10<sup>5</sup>–10<sup>6</sup> y.

At Narra in the Philippines, ongoing interactions between clastic sediments and Ca-OH-type alkaline fluids (pH >11) have been observed (Shimbashi *et al.*, 2018). The sediments originated from a combination of serpentinized rocks and gabbro, and deposition of the sediments began 15,000 y ago (Shimbashi *et al.*, 2020). The depositional environment of the sediments probably changed from seawater to freshwater over time, resulting in different species of secondary phases depending on the depositional environment. Specifically, dioctahedral nontronite with part of an interlayer hydroxide sheet was formed, presumably by interactions between the sediments and alkaline fluid interaction with the involvement of seawater (Shimbashi *et al.*, 2020; Shimbashi *et al.*, 2022b). When the depositional environment changed to freshwater, 14 Å tobermorite and trioctahedral Fe- and Mg-bearing clays were formed through a similar interaction without seawater infiltration (Shimbashi *et al.*, 2020). The trioctahedral Fe- and Mg-bearing clays consisted of tetrahedral–octahedral–tetrahedral layers, imperfect interlayer hydroxide sheets, and interlayer Ca ions. Mineralogical changes, such as the gradual decrease of the interlayer hydroxide sheets, occurred during the interaction. Furthermore, the Fe- and Mg-bearing clays probably oxidized after sample collection (Shimbashi *et al.*, 2022b).

In Voltri Massif, Italy, interactions between serpentinites and alkaline fluids with a pH of 11.8–12.3 (from a spring named BR1) resulted in the formation of saponite and sepiolite, which precipitated together with or replaced serpentine (Schwarzenbach *et al.*, 2013).

In the Samail Ophiolite in Oman, calcite was precipitated owing to the uptake of atmospheric CO<sub>2</sub> and evaporation in Ca-OH water pools (pH >11.6; Giampouras *et al.*, 2020).

**Table 2.** Secondary phases near pyrometamorphic rocks and with Ca-OH-type alkaline fluids in ophiolites

Setting	Type	Site	Chemical reaction condition	Time	Secondary phases	Reference
Pyrometamorphic rocks	Ca-OH	Maqarin, Jordan	Interaction between biomicrite host rock and alkaline water	—	C–A–S–H Ettringite Thaumasite Calcite Si–Al–rich gels Chabasite (*precipitated downstream in low-pH regions)	Martin <i>et al.</i> (2016)
Ophiolite	Ca-OH	Luzon Island, the Philippines	Interaction between bentonite and alkaline water	—	Chrysotile Clinoptilolite Heulandite Silica minerals K-feldspar Pyrite Nontronite Calcite	Fujii <i>et al.</i> (2014)
		Parsata, Cyprus	Interaction between bentonite and alkaline water	10 <sup>5</sup> –10 <sup>6</sup> y	Fe-bearing palygorskite	Milodowski <i>et al.</i> (2016)
		Narra, the Philippines	Interaction between clastic sediments derived from serpentinite and gabbro and alkaline water	<10,000 y	14 Å Tobermorite Fe- and Mg-bearing clays which comprised TOT layers, imperfect interlayer hydroxide sheets, and interlayer Ca ions	Shimbashi <i>et al.</i> (2020, 2022b)
			Interaction between clastic sediments derived from serpentinite and gabbro and alkaline water with the involvement of seawater	<15,000 y	Nontronite with parts of interlayer hydroxide sheets	Shimbashi <i>et al.</i> (2020, 2022b)
		Voltri Massif, Italy	Interaction between serpentinites and alkaline water	—	Saponite Sepiolite Serpentine	Schwarzenbach <i>et al.</i> (2013)
		Samail Ophiolite, Oman	Interaction with air or evaporation of spring water	—	Calcite	Giampouras <i>et al.</i> (2020)

### Mg-HCO<sub>3</sub> type

In the Samail Ophiolite in Oman, various hydrated magnesium (hydroxy) carbonates have been recognized in Mg-HCO<sub>3</sub>-type alkaline fluids (7.9 < pH < 9.5; Giampouras *et al.*, 2020). Nesquehonite was formed via evaporation and was transformed into dypingite and hydromagnesite. In addition, the low-temperature alteration of partially serpentinized, less-altered peridotites was reported by Mayhew *et al.* (2018). It is presumed that the alteration occurred via interactions with Mg-HCO<sub>3</sub>-type alkaline fluids (pH ~8). The alteration included the loss of olivine and Fe(II)-bearing brucite, an increase in the oxidized iron content in the serpentine, and the appearance of Fe(III) hydroxides and carbonate. It was also indicated that chromite was altered to Cr-rich magnetite and subsequently to chlorite at low temperatures.

In the Kamuikotan tectonic belt in Japan, the mixing of Mg-HCO<sub>3</sub>-type alkaline seepage with a pH of 10.34 and Mg-HCO<sub>3</sub>-type alkaline surface water with a pH of 9.69 produced layered double hydroxide (LDH) (Nishiki *et al.*, 2020). In contrast, the mixing of Ca-bearing Mg-HCO<sub>3</sub>-type alkaline seepage with a pH of 10.67 and Mg-HCO<sub>3</sub> type-alkaline surface water with a pH of 9.57 produced aragonite. In addition to LDH and aragonite, the formation of magnesium silicate hydrate (M–S–H), considered low-crystalline chrysotile, has also been reported.

In northern Southland, New Zealand, debris flowing from an ophiolite mélange was deposited <7000 y ago (Craw *et al.*, 1987). The interaction between detrital debris flows and alkaline fluids

with pH 9 under reducing conditions produced Fe-bearing chrysotile and nanocrystalline alumina (probably pseudoboehmite) in the veins. They often coexisted with calcite as a vein mineral, and magnetite and pyrite were recognized near and adjacent to the veins.

In Norway, the Feragen ultramafic body is covered with felsic glacial sediments mixed with ultramafic rock fragments. It has been reported that the dissolution of quartz in sediments and the evaporation process leads to the precipitation of amorphous silica, which subsequently reacts with Mg-HCO<sub>3</sub>-type alkaline fluids (pH ~10) to precipitate M–S–H (De Ruiter *et al.*, 2021). The Mg:Si ratio of the M–S–H is between 0.9 and 1.1. M–S–H, which is assumed to be precipitated via association with the dissolution of K-feldspar, contains slightly more Al (De Ruiter and Austrheim, 2018).

At the Leka Ophiolite Complex in Norway, Mg-HCO<sub>3</sub>-type groundwater (8.2 < pH < 9.4) was recognized (Okland *et al.*, 2012). It was produced by the dissolution of serpentine, brucite, and calcite and the precipitation of chrysotile and hydromagnesite. The hydromagnesite coexisted with small amounts of aragonite. Moreover, the dissolution of Fe(II)-bearing brucite and the formation of iron hydroxide is presumed.

### Mix type

In the Samail Ophiolite in Oman, mix-type water pools (9.6 < pH < 11.5) were recognized, and aragonite was predominantly formed

**Table 3.** Secondary phases with Mg-HCO<sub>3</sub>-type and mix-type alkaline fluids in ophiolites

Setting	Type	Site	Chemical reaction condition	Time	Secondary phases	Reference
Ophiolite	Mg-HCO <sub>3</sub>	Samail Ophiolite, Oman	Interaction with air or evaporation of spring water	—	Hydrated magnesium (hydroxy-) carbonate phases	Giampouras <i>et al.</i> (2020)
		Samail Ophiolite, Oman	Low-temperature alteration and hydration of partially serpentinized peridotites	—	Fe(III)-hydroxides Carbonate Magnetite Chlorite	Mayhew <i>et al.</i> (2018)
		Kamuikotan tectonic belt, Japan	Mixing Mg-HCO <sub>3</sub> type seepage and Mg-HCO <sub>3</sub> type surface water	—	LDH Aragonite M-S-H (low-crystalline chrysotile)	Nishiki <i>et al.</i> (2020)
		Northern Southland, New Zealand	Interaction between detrital debris flows from ophiolite melange and alkaline water under reducing conditions	<7000 y	Fe-bearing chrysotile Non-crystalline alumina Calcite Magnetite Pyrite	Craw <i>et al.</i> (1987)
		Feragen ultramafic body, Norway	Interaction between glacial till and alkaline water	—	M-S-H	De Ruiter and Austrheim (2018); De Ruiter <i>et al.</i> (2021)
		Leka Ophiolite Complex, Norway	Ongoing low-temperature water-rock processes in partially serpentinized dunite	—	Chrysotile Hydromagnesite Iron hydroxide Aragonite	Okland <i>et al.</i> (2012)
Mix	Mix	Samail Ophiolite, Oman	Interaction with air or evaporation of spring water	—	Aragonite Calcite Brucite LDH	Giampouras <i>et al.</i> (2020)
		Bat and Hilti, Oman	Mixing Ca-OH type spring water and Mg-HCO <sub>3</sub> type river water	—	Aragonite Calcite Brucite LDH M-S-H	Anraku <i>et al.</i> (2017)

due to the uptake of atmospheric CO<sub>2</sub> and evaporation (Giampouras *et al.*, 2020). Calcite, brucite, and trace LDH phases were occasionally attached to aragonite.

At Bat and Hilti in Oman, the mixing of Ca-OH-type spring water (pH >11) and Mg-HCO<sub>3</sub>-type river water (8.46 < pH < 8.59) produced carbonate, LDH, and brucite (Anraku *et al.*, 2017). The mineral species of carbonate are determined by dissolved Mg ions, which vary with the mixing ratio of river water to spring water. Specifically, calcite is recognized near Ca-OH-type springs and aragonite at locations where Mg-HCO<sub>3</sub>-type river water is highly mixed. LDH was formed in areas with Ca-OH-type spring water which is relatively rich in Al ions, and brucite was formed in areas with Ca-OH-type spring water which is relatively poor in Al ions. Furthermore, the formation of M-S-H has been speculated about (Anraku *et al.*, 2017).

#### Alkaline saline lake

At Teels Marsh, Nevada, an alkaline saline lake with tuffaceous sediments has been reported (Taylor and Surdam, 1981). The pH of the brine ranged from 9 to 10. The interaction between rhyolitic glass and alkaline brines produced hydrous alkali aluminosilicate gel and then formed phillipsite within 1000 y. Analcime was also found to be associated with the phillipsite, indicating that it was formed by the reaction of phillipsite with Na<sup>+</sup>-rich brines. Clinoptilolite was detected only in trace amounts. In addition to

phillipsite and analcime, gaylussite and searlesite have been reported as common authigenic phases.

In Searles Lake in California, lacustrine sediments deposited over 3.2 million y have been investigated (Hay and Guldman, 1987; Hay *et al.*, 1991). The drill core, which consisted of 693.4 m of sediments, was divided into three diagenetic zones. In the upper zone (0–291.1 m), detrital montmorillonite and kaolinite reacted with pore water (alkaline brine with a pH of 9–10) to form Mg-smectite, Fe-illite, K-feldspar, and analcime (Hay *et al.*, 1991). Phillipsite was recognized at a depth of 19.9 m. In the middle zone (291.1–541.6 m), detrital montmorillonite was probably the major reactant and formed smaller amounts of the same authigenic silicates as those in the upper zone, as the pH of the pore water was lower than that in the upper zone, but still probably exceeded 9. K-feldspar crystallized within ~42,000 y (Hay *et al.*, 1991). In the lower zone (541.6–693.4 m), vitric ash reacted with the pore water (pH 7.5–8) at 45–85°C, and the formation of montmorillonite, clinoptilolite, anhydrate, and a trace of opal was identified (Hay and Guldman, 1987; Hay *et al.*, 1991). The lowermost samples also contained analcime, probably indicating that the clinoptilolite was replaced by analcime (Hay and Guldman, 1987).

In the Colorado Plateau in New Mexico, authigenic minerals were formed in alkaline saline lakes owing to the low-temperature alteration of silicic ash deposited during late-Jurassic volcanism (Turner and Fishman, 1991). Around the margins of the lakes,



**Table 4.** Secondary phases in alkaline saline lakes

Setting	Type	Site	Chemical reaction condition	Time	Secondary phases	Reference
Alkaline saline lake	Rich in Na or K	Lake Teels Marsh, Nevada	Lake with rhyolitic glass	<1000 y for Phillipsite formation	Hydrous alkali aluminosilicate gel Phillipsite Analcime Clinoptilolite Gaylussite Searlesite	Taylor and Surdam (1981)
	Rich in Na or K	Lake Searles, California	Lake with vitric ash —Montmorillonite —Kaolinite —Illite	<3,200,000 y <42,000 y for K-feldspar formation	Mg-rich smectite Fe-rich illite K-feldspar Analcime Phillipsite Clinoptilolite Montmorillonite Anhydrite Opal	Hay and Goldman (1987); Hay <i>et al.</i> (1991)
	Rich in Na or K	Lake T' oo' dichi', Colorado Plateau	Lake with silicic volcanic ash	<Jurassic	Smectite Clinoptilolite Analcime K-feldspar Mixed-layer illite-smectite Chlorite Quartz Chalcedony Albite	Turner and Fishman (1991)
	Rich in Na or K	Paleo-lake Olduvai, Olduvai	Lake with volcanic ash	—	Al-rich smectite Mg, Fe, and Ti-rich smectite Chabazite Phillipsite K-feldspar	McHenry (2010)
	Rich in Na or K	Lake Albert, Oregon	Lake with weathered pyroclastic rocks —Montmorillonite —Montmorillonite/illite —Montmorillonite/intergrade smectite-chlorite interstratification	—	Interstratified illite and a trioctahedral, Mg-rich mineral resembling stevensite in composition	Jones and Weir (1983)
	Rich in Na or K	Salina Verde, Brazil	Soil surrounding the lake	—	Trioctahedral smectite (saponite, and stevensite) Diocahedral mica (glaucanite, Fe-illite, and illite) Si-rich amorphous materials Ferri-beidellite	Furquim <i>et al.</i> (2008); Furquim <i>et al.</i> (2010); Barbiero <i>et al.</i> (2016)
	Rich in Na or K	Lake Yoa, Chad	—	—	Stevensite Amorphous silica Aragonite Various salts	Darragi and Tardy (1987)

where the pore waters are recharged, smectite was recognized as an authigenic mineral. In addition to smectite, clinoptilolite was identified in the central region of the lakes adjacent to these locations. The clinoptilolite is believed to have formed directly from silicic ash. Adjacent to this, but near the center of the lake, analcime, K-feldspar, mixed-layer illite-smectite with variable composition (0–100% expandable layers), chlorite, quartz, and chalcedony were recognized. As the authigenic K-feldspar overgrew on chlorite, it is suggested that the chlorite may have formed earlier than K-feldspar. In the center-most part of the lake, albite, mixed-layer illite-smectite in highly illitic layers (typically 0–30% expandable layers), chlorite, quartz, and chalcedony were recognized. These distributions are attributed to a lateral

hydrogeochemical gradient characterized by an increase in pH and salinity owing to the interaction with lacustrine sediments and water.

In the alkaline saline lake of the Olduvai paleolake, a change in the distribution of authigenic minerals toward the center of the lake has also been reported (McHenry, 2010). In the distal lake margin, the smectitic clay minerals were dominated as authigenic minerals with some zeolite. The alteration of the volcanic glass caused an increase in the salinity and alkalinity of the fluids, which led to the initial formation of clay minerals. Chabazite and phillipsite were dominant at the proximal margins. As the salinity and alkalinity fluctuated with the lake water level, chabazite and phillipsite nucleated on the clay surfaces. In the lake center, where the pH of

the fluids was high and the  $K^+$  activity was strong, phillipsite and K-feldspar were dominant. Although clay minerals were preserved in the proximal margin and lake center, the chemical components of the clay minerals differed from those in the distal lake margin. In the distal lake margin, where the clay minerals were dominant, they were more Al-rich. In contrast, the clay minerals were rich in Mg, Fe, and Ti in the proximal margin and lake center, where zeolite dominated.

Lake Abert in Oregon is an alkaline saline lake with a pH of 9.7 (Phillips and Van Denburgh, 1971). Volcanic rocks, ranging from basalt to rhyolite, weathered to give a range of clays, including montmorillonite, montmorillonite/illite, and montmorillonite/intergrade smectite–chlorite interstratified clays, which entered the lake as detritus (Jones and Weir, 1983). These detrital clays were modified by interactions with the alkaline saline water to form authigenic interstratified illite and a trioctahedral, Mg-rich mineral resembling stevensite in composition (Jones and Weir, 1983).

The distribution of clay minerals has been investigated in the soils surrounding an alkaline saline lake in the Pantanal Wetland, Brazil (Furquim *et al.*, 2008; Furquim *et al.*, 2010; Barbiero *et al.*, 2016). The soil pH ranged from 9.2 to 10.9. A zone rich in authigenic trioctahedral smectite was found in the topsoil close to the lake, where Fe and Al ions were bonded to organic colloids, preventing these ions from contributing to the formation of mica. In contrast, a zone rich in authigenic dioctahedral mica was found in deeper horizons, a few meters apart, where the mineralization of organic matter and release of available Fe and Al ions allowed for the formation of the mica (Barbiero *et al.*, 2016). The authigenic trioctahedral smectites in the topsoil close to the lake were referred to as saponitic and stevensitic minerals based on differences in their Al content; they were formed by direct precipitation from the water (Furquim *et al.*, 2008). The authigenic dioctahedral micas in the deeper horizons, a few meters away from the lake, were  $Fe^{3+}$ -rich micas (Fe-illite, and glauconite) with small amounts of illite. They coexist with Si-rich amorphous materials and are believed to be neoformed (Furquim *et al.*, 2010). Moreover, some of them transformed into ferribeidellite owing to the wetting-drying cycles (Furquim *et al.*, 2008).

Lake Yoa in Chad is an alkaline saline lake with a pH >9.3 (Darragi and Tardy, 1987). At this site, the formation of stevensite and aragonite, in addition to the formation of various salts, has been observed. Stevensite is associated with amorphous silica.

### Implications for cement–bentonite interactions in radioactive waste repositories

#### Formation conditions and mineralogical transition of secondary phases

In the previous section, secondary phases reported to occur at natural sites were summarized. In this section, the following secondary phases were selected, and their formation conditions and mineralogical transition in radioactive waste repositories are discussed based on the findings in the previous section, as well as laboratory and *in situ* experiments.

#### Calcium silicates

The formation of 14 Å tobermorite was observed near ophiolites where Ca-OH-type alkaline fluids are present (Shimbashi *et al.*, 2020). This indicates that 14 Å tobermorite can potentially form during the alteration of bentonite close to cementitious materials with Stage I and II alkaline leachates (Table 5). Contrary to this,

**Table 5.** List of secondary phases suggested by NA studies at various geological settings

Setting	Type	Analogous to waste repositories	Secondary phases
Pyrometamorphic rocks		Alteration of bentonite close to cementitious materials with Stage I and II alkaline leachates	<u>Calcium silicates</u> C–A–S–H <u>Aluminum silicates</u> Si–Al-rich gel <u>Carbonates</u> Calcite <u>Sulfates</u> Ettringite Thaumassite
Ophiolite	Ca-OH		<u>Calcium silicates</u> 14 Å tobermorite <u>Aluminum silicates</u> Clinoptilolite Heulandite K-feldspar <u>Magnesium or iron silicates</u> Chrysotile Nontronite (with partial interlayer of hydroxide sheets) Fe-bearing palygorskite Fe- and Mg-bearing clays which comprise TOT layers, imperfect interlayer hydroxide sheets, and interlayer Ca ions Saponite Sepiolite <u>Carbonates</u> Calcite <u>Others</u> Silica minerals Pyrite
Mg-HCO <sub>3</sub>		Alteration of bentonite located farther from cementitious materials and rich in Mg <sup>2+</sup> ions	<u>Magnesium or iron silicates</u> (Fe-bearing) chrysotile M–S–H Chlorite <u>Carbonates</u> Hydrated magnesium (hydroxy) carbonate phases Aragonite Calcite <u>Others</u> LDH Non-crystalline alumina Magnetite Pyrite Iron-hydroxide
Mix		Alteration of bentonite located at intermediate sites where Ca-OH-type and Mg-HCO <sub>3</sub> -type are similar to bentonite, respectively.	<u>Magnesium or iron silicates</u> M–S–H? <u>Carbonates</u> Aragonite Calcite <u>Others</u> Brucite LDH
Alkaline saline lake		Alteration of bentonite farther from the cementitious material interface	<u>Aluminum silicates</u> Hydrous alkali aluminosilicate gel Phillipsite Analcime Clinoptilolite Chabazite

(Continued)

Table 5. (Continued)

Setting	Type	Analogues to waste repositories	Secondary phases
			Al-rich smectite
			Albite
			K-feldspar
			Mixed-layer illite-smectite
			Magnesium or iron silicates
			Mg- (Fe- and Ti-) rich smectite
			Fe-rich illite
			Chlorite
			Glauconite
			Ferribeidellite
			<u>SiO<sub>2</sub> minerals</u>
			Opal
			Quartz
			Chalcedony
			Amorphous silica
			<u>Others</u>
			Gaylussite
			Searlesite
			Anhydrite
			Aragonite

the formation of 14 Å tobermorite has not been reported in previous laboratory and *in situ* experiments showing alkaline alteration of bentonite or clay, but rather the formation of C–S–H, C–A–S–H, 11 Å tobermorite, or Al–tobermorite (Fernández *et al.*, 2016; Lalan *et al.*, 2016; Fernández *et al.*, 2017; Lerouge *et al.*, 2017; Nakarai *et al.*, 2021; Ramírez *et al.*, 2005; Sánchez *et al.*, 2006; Yokoyama *et al.*, 2011; Techer *et al.*, 2012). The tendency for C–S–H to form at low temperatures was recognized from these experiments, which lasted up to 15 y (Appendix A in the Supplementary material). This may be due to metastable C–S–H formation instead of 14 Å tobermorite in the short term and formation of stable 14 Å tobermorite with a slower precipitation rate in the long term because it is known that C–S–H with a Ca:Si ratio of <1.4 is a 14 Å tobermorite with an incomplete crystal structure (Taylor, 1997). According to natural geochemical reactions, the formation of 14 Å tobermorite has occurred within 10,000 y (Shimbashi *et al.*, 2020). Therefore, it is implied that the time required for the formation of 14 Å tobermorite may be more than a few decades but less than a few thousand years at low temperatures. As it is estimated that Stage I can last approximately 10,000 y and Stage II can last from 10,000 to 200,000 y (Sun *et al.*, 2022 and references therein), the mineralogical transition from C–S–H to 14 Å tobermorite may need to be considered in RT modeling for the performance assessment of bentonite in radioactive waste repositories.

The formation of 11 Å tobermorite was not recognized from natural geochemical reactions at low temperatures (Table 5), while they were reported in previous laboratory and *in situ* experiments at >70°C (Appendix A in the Supplementary material). It is known that three types of tobermorite exist in different degrees of hydration: 14 Å tobermorite (plombierite), 11 Å tobermorite, and 9 Å tobermorite (riversideite), from most hydrated to least hydrated (McConnell, 1954). Furthermore, 14 Å tobermorite transforms to 11 Å tobermorite by heating at 90°C, and subsequent heating at 300°C causes lattice shrinkage to form 9 Å tobermorite, although some 11 Å tobermorite does not shrink (Mitsuda and Taylor, 1978). Therefore, 11 Å tobermorite and 9 Å tobermorite may not form at temperatures of <~70°C.

C–A–S–H was recognized at sites near pyrometamorphic rocks, indicating that C–A–S–H can potentially form during the alteration of bentonite close to cementitious materials with Stage I and II alkaline leachates (Table 5). This is consistent with previous laboratory and *in situ* experiments demonstrating C–A–S–H formation during the alkaline alteration of bentonite or clay (Yokoyama *et al.*, 2011; Fernández *et al.*, 2016; Lalan *et al.*, 2016; Fernández *et al.*, 2017). In addition, laboratory and *in situ* experiments exhibited the tendency for the secondary phases to change from C–A–S–H to Al–tobermorite with increasing temperature (Appendix A in the Supplementary material). This tendency may be due to metastable C–A–S–H formation instead of Al–tobermorite at low temperatures and stable Al–tobermorite formation within a shorter time at higher temperatures. It is worth noting that Al–tobermorite formations have been reported within 16.5 y in cementitious materials at 40–55°C (Maruyama *et al.*, 2021) and within 2000 y in Roman concrete that reacted with seawater at low temperatures (Jackson *et al.*, 2017). Therefore, a mineralogical transition from C–A–S–H to Al–tobermorite may also need to be considered in RT modeling for the performance assessment of bentonite, even at low temperatures.

As described above, C–S–H, C–A–S–H, 14 Å tobermorite, and Al–tobermorite have been suggested to occur under alkaline conditions from Stage I and II leachates at low temperatures in radioactive waste repositories. On the other hand, these secondary phases have not been reported to form under lower pH conditions. Therefore, they are likely to become unstable after a decrease in pH over time in radioactive waste repositories.

#### Zeolite (aluminum silicates)

In alkaline lakes, species of zeolite tend to depend on the pH conditions. Specifically, phillipsite was observed under relatively high pH conditions, while clinoptilolite and chabazite were observed under relatively low pH conditions. Analcime tends to form under relatively high pH conditions though it can form under relatively low pH conditions when following clinoptilolite formation (Hay and Guldman, 1987). It has been reported that an increase in pH reduces the Si/Al ratio of the solution, resulting in the formation of zeolite with low Si/Al ratios, such as phillipsite and analcime, rather than zeolite with a high Si/Al ratio, such as clinoptilolite (Mariner and Surdam, 1970). Therefore, the tendency to form phillipsite and analcime under relatively high pH conditions and clinoptilolite under relatively low pH conditions in alkaline lakes may be influenced by the Si/Al ratios of the fluids. On the contrary, chabazite formed under relatively low pH conditions despite the low Si/Al ratio. Although the conditions that determine the formation of clinoptilolite and chabazite are unknown, the formation of zeolite in alkaline saline lakes suggests that it can potentially form during bentonite alteration farther from the interface between cementitious materials and bentonite, where the chemistry of alkaline saline lake is analogous in radioactive waste repositories (Fig. 5). Furthermore, the distribution of zeolite species even within the locations that are analogous to the chemistry of alkaline saline lake (Fig. 5) is suggested to be dependent on pH conditions.

Several previous laboratory and *in situ* experiments have reported phillipsite or analcime formation owing to the alkaline alteration of bentonite or clay (Bauer and Velde, 1999; Vigil de la Villa *et al.*, 2001; Ramírez *et al.*, 2002; Ramírez *et al.*, 2005; Sánchez *et al.*, 2006; Yokoyama and Nakamura, 2010; Lalan *et al.*, 2016), indicating that they have the potential to form during the alteration of bentonite close to cementitious materials with Stage I and II

alkaline leachates. Compared with the laboratory and *in situ* experiments, pH conditions under which phillipsite and analcime are formed in alkaline saline lakes are relatively low. These facts indicate that the phillipsite and analcime formed under alkaline conditions from Stages I and II leachates could be stable, even after a decrease in pH over time.

The formation of phillipsite is followed by the formation of analcime in an alkaline saline lake in Teels Marsh (Taylor and Surdam, 1981). On the other hand, laboratory experiments showed a tendency for the secondary phases to change from phillipsite to analcime with increasing temperature or interaction time. For example, laboratory experiments under a wide range of temperature conditions show that phillipsite is formed at lower temperatures (75°C) and analcime at higher temperatures (125–200°C) (Sánchez *et al.*, 2006). In a laboratory experiment conducted at 90°C, phillipsite was observed after 30 days, and analcime, in addition to phillipsite, was observed after 90 days (Ramírez *et al.*, 2002). The tendency indicates the metastable phase of phillipsite and the stable phase of analcime under those conditions. However, the timescales required for these mineral transitions differ depending on the conditions. In particular, while laboratory experiments have reported the formation of analcime within 1 year at low temperatures (23–60°C) (Yokoyama and Nakamura, 2010), the formation of phillipsite has been reported to occur within 1000 y in alkaline saline lakes, followed by the formation of analcime (Taylor and Surdam, 1981). These different timescales for analcime formation may be caused not only by different temperature conditions but also by different pH and other chemical concentrations; for example, the mineralogical transition in the laboratory experiments at pH 14 was relatively rapid, whereas that in the alkaline saline lakes at pH 9–10 was relatively slow. Because the pH and other chemical concentrations expected in the radioactive waste repositories vary over time and space, it is important to consider temporal and spatial chemical conditions in bentonite when predicting the timescale of the mineralogical transition of zeolite mineral species. Despite the different time scales, considering a mineralogical transition of zeolite mineral species may be important in RT modeling for the performance assessment of bentonite.

#### *Magnesium silicates*

In several laboratory experiments wherein bentonite or clay interacted with alkaline fluids, NaOH, Ca(OH)<sub>2</sub> and KOH were often used as alkaline fluids based on the simplified composition of pore waters from cementitious materials over time, and calcium silicates and zeolite formation was reported (Ramírez *et al.*, 2005; Yokoyama *et al.*, 2011). On the other hand, in natural environments with the presence of Mg, Mg-bearing smectite (i.e. smectite enriched in structural Mg such as saponite) was detected at sites with Ca-OH-type alkaline fluids near ophiolites (Table 5). This indicates their potential formation during the alteration of bentonite close to cementitious materials with Stage I and II alkaline leachates. This was consistent with previous laboratory experiments that considered the Mg effect and *in situ* experiments showing Mg-bearing smectite formation during the alkaline alteration of bentonite or clay (Fernández *et al.*, 2009; Lerouge *et al.*, 2017; Sánchez *et al.*, 2006). As Mg-bearing smectite formation was also observed under moderately alkaline conditions in alkaline saline lakes (Table 5), it is suggested that Mg-bearing smectite, which forms under alkaline conditions from Stage I and II leachates in radioactive waste repositories, could be

stable even after a decrease in pH over time. Furthermore, this indicates that Mg-bearing smectite can potentially form during bentonite alteration farther from the interface between cementitious materials and bentonite in radioactive waste repositories.

A smectitic phase with imperfect interlayer hydroxide sheets was also found at sites with Ca-OH-type alkaline fluids near ophiolites (Table 5), suggesting that it can potentially form during bentonite alteration close to cementitious materials with Stage I and II alkaline leachates in radioactive waste repositories. This was consistent with previous laboratory and *in situ* experiments. For example, in *in situ* experiments on cementitious materials and clay rocks, the formation of Mg-bearing smectite with Mg(OH)<sub>2</sub> in the interlayer was discussed (Lerouge *et al.*, 2017). In addition, intercalation of Mg(OH)<sub>2</sub> in the montmorillonite interlayer has been observed in laboratory and *in situ* experiments (Fernández *et al.*, 2009; Fernández *et al.*, 2013; Cuevas *et al.*, 2018; Fernández *et al.*, 2018). As it is known that the intercalation of Mg(OH)<sub>2</sub> in the montmorillonite interlayer easily occurs at pH values between 10 and 12 (Xeidakis, 1996), the hydroxide sheets in the interlayer could occur under alkaline conditions from Stage I and II leachates and would be unstable after a decrease in pH over time in radioactive waste repositories.

M–S–H was recognized at sites with Mg-HCO<sub>3</sub>-type alkaline fluids near ophiolites (Table 5), suggesting that it can potentially form during bentonite alteration farther from the interface between cementitious materials and bentonite in radioactive waste repositories. On the other hand, in previous *in situ* experiments, M–S–H formed during the alkaline alteration of clay rocks (Dauzères *et al.*, 2016; Bernard *et al.*, 2020). The M–S–H formation was implied to form in clay rocks away from the interface of Portland cement paste (Bernard *et al.*, 2020). This is consistent with the above discussion that M–S–H could be formed by the alteration of bentonite farther from the interface between cementitious materials and bentonite. Notably, the structure of M–S–H is similar to that of Mg-bearing phyllosilicates (Roosz *et al.*, 2015; Nied *et al.*, 2016; Pedone *et al.*, 2017), and M–S–H could be the precursor of the Mg-bearing phyllosilicates, such as smectite, talc, or serpentine (Roosz *et al.*, 2015; Nied *et al.*, 2016). Their structural similarity makes it difficult to distinguish M–S–H from other Mg-bearing phyllosilicates after several years of interaction. Indeed, for the same samples after a 4.9-year interaction between cementitious materials and clay rocks, M–S–H formation was reported by Dauzères *et al.* (2016), while that of Mg-bearing smectite was reported by Lerouge *et al.* (2017). Therefore, distinguishing between M–S–H and Mg-bearing phyllosilicates and understanding the time scales required for their mineralogical transition is a future challenge. In addition, it is important to clarify which Mg-bearing phyllosilicates will form after the mineralogical transition of M–S–H in a given condition because permeability is expected to change depending on the swelling smectite or non-swelling minerals, such as talc and serpentine.

#### *Summary*

Comparison between the findings of secondary phases compiled in this review and findings in previous laboratory and *in situ* experiments provide an implication for the species and mineralogical transition of secondary phases that have the potential to form during cement–bentonite interactions. Specifically, C–S–H, C–A–S–H, and phillipsite were suggested as potential secondary phases, and the mineralogical transition from

C–S–H to 14 Å tobermorite, C–A–S–H to Al–tobermorite, and phillipsite to analcime may need to be considered during the alteration of bentonite close to cementitious materials with Stage I and II alkaline leachates at low temperatures. After a decrease in pH over time, 14 Å tobermorite and Al–tobermorite would be unstable, while analcime would be stable. Mg-bearing smectite and a smectitic phase with imperfect interlayer hydroxide sheets were also potential secondary phases during the alteration of bentonite close to cementitious materials with Stage I and II alkaline leachates. Note that M–S–H may be the precursor to Mg-bearing phyllosilicates such as Mg-bearing smectite. When the pH decreased over time, Mg-bearing smectite would be stable, while a smectitic phase with imperfect interlayer hydroxide sheets would be unstable.

During bentonite alteration farther from the interface between cementitious materials and bentonite, phillipsite, analcime, clinoptilolite, chabazite, newly formed Mg-bearing smectite, and M–S–H were indicated as potential secondary phases. Among those minerals, phillipsite would form under relatively high pH conditions, which may depend on the distance from the cementitious materials, while clinoptilolite and chabazite would form under relatively low pH conditions. The mineralogical transition from phillipsite to analcime would occur, although the time scale required for the transition would be slower than that close to the cementitious materials. Furthermore, the mineralogical transition from clinoptilolite to analcime may also occur.

## Conclusion

Understanding the cement–bentonite interactions is important to evaluate bentonite properties in radioactive waste repositories. Investigating natural geochemical reactions has the significant advantage of observing geochemical reactions over a long period of time. In this review, the secondary phases formed at low temperatures (<100°C) and under alkaline conditions were compiled for a broader range of natural sites than in previous reviews. Specifically, studies reporting secondary phases near pyrometamorphic rocks, near ophiolites, and in alkaline saline lakes, were summarized. Furthermore, this review provides implications for the species and mineralogical transition of secondary phases formed by the spatiotemporal alteration of bentonite by adding that information from natural sites to previous laboratory and *in situ* experiments. This will be useful for selecting secondary phases to be considered in the RT modeling for performance assessment of bentonite by comparing the secondary phases predicted to form by the RT modeling and insights from this review.

**Supplementary material.** The supplementary material for this article can be found at <https://doi.org/10.1017/cmn.2024.4>.

**Data availability statement.** The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request. Code availability: not applicable.

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