

## Review papers

# Theoretical and earthquake-induced groundwater chemistry changes: A perspective

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## ABSTRACT

To minimize the loss of life caused by earthquakes, it is crucial to have early warning tools that provide sufficient warning time. Although various methods are available, their accuracy is uncertain. This review explores alternative indicators related to hydrogeochemical anomalies that appear before earthquakes, which could potentially offer earlier warnings. It presents a theoretical basis for ionic and molecular changes initiated by the generation of hydroxyl radicals ( $\bullet\text{OH}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in groundwater before an earthquake. The review analyses 32 earthquake events by measuring ionic anomalies through standard reduction potential. The study also identifies significant pre-seismic erosional activity in minerals exposed to hydrogen peroxide. Additionally, the oxidation of organic compounds is shown to predict notable geochemical changes. The changes in the groundwater chemistry can also be validated by examining simultaneous microbial/ zooplankton responses. The findings suggest that the ionic, mineral, organic, and microbiological changes triggered by hydroxyl radicals and hydrogen peroxide could serve as a multi-parametric earthquake early-warning system. Implementation of such a system could improve the accuracy and timeliness of earthquake warning systems potentially reducing the associated risks and damages.

## 1. Introduction

Efforts to forecast earthquakes have been ongoing for decades, yet an effective short-term prediction method remains undeveloped. While traditional approaches focused on seismic or fault mechanics to identify precursory phenomena, recent research has shifted toward non-seismic indicators. A variety of non-seismic precursors are being investigated, such as changes in groundwater chemistry (Barberio et al., 2017; Malakootian & Nouri, 2010; Skelton et al., 2008), induction of electric and magnetic fields (Ohta et al., 2001; Nagao et al., 2002), anomalous gas emissions (Ghosh et al., 2009), changes in infrared radiation (Panda et al., 2007; Saraf et al., 2008), and changes in surface potentials (Balk et al., 2009). Despite these studies, earthquake events remain unpredictable because of uncertainties in understanding the generation of

different types of precursors, their variability, and their tendency to overlap with non-seismic factors (Paudel et al., 2018). A multi-parametric approach is necessary for successful short-term predictions and for developing an early warning system. Multi-parametric approach-based earthquake early warning system constitutes the coordinated study of multiple parameters/precursors observed before an earthquake. This involves the combination of all precursors: gases (both in groundwater (below) and atmosphere and ionosphere (above)), variations in electromagnetic fields, chemical compositions, isotopic ratios, strain accumulation, and so on. This paper reviews groundwater chemistry anomalies that are most often associated with seismic activity in the hope that this can aid in developing a multi-parametric based earthquake early warning system.

During the 1980 s and 1990 s, several studies investigated the

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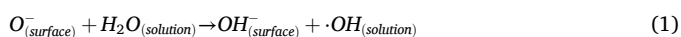
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chemistry and behavior of peroxy defects in igneous and metamorphic rocks (Freund, 1987; Freund et al., 1989; Freund et al., 1993; Kathrein & Freund, 1983). Chemically, peroxy links are characterized by covalent bonds and short distances and represent point defects in the sublattice of oxide materials. Normally dormant and electrically inactive, these bonds can produce reactive oxygen species (ROS) when stressed at rock-water interfaces, such as weathered mineral surface and rock faulting. Stress on peroxy links in silicate minerals during mechanical deformation can break the –OO– (peroxy bond) to form reactive oxygen species,  $O^{\bullet}$  (Balk et al., 2009). Consequently, defect electrons are produced in the  $O^{2-}$  or  $[SiO_4]_4$  matrix. This discovery introduced a new semiconductor aspect to the electrical properties of rocks and minerals.

In these materials, oxygen can exist in two valence states:  $O^{\bullet}$  and  $O^{2-}$ .  $O^{2-}$  has a stable outer electronic shell, while  $O^{\bullet}$  has one less electron and isoelectronic with fluorine. In an  $O^{2-}$  matrix, the presence of  $O^{\bullet}$  represents a lattice defect or a hole (denoted as  $h^{\bullet}$ ), which is a positively charged lattice site within the  $O^{2-}$  matrix. These positive holes can act as charge carriers in oxide materials like MgO and silicate minerals, inducing electronic conductivity in an otherwise insulating matrix predominantly composed of  $O^{2-}$  (Freund et al., 1993). When peroxy bonds break, the holes and electron charge carriers are generated within the stressed crystal lattice (Freund, 2002; Freund, 2003). These  $h^{\bullet}$  propagate from the stressed region to the unstressed region, making stressed regions negatively charged and unstressed regions positively charged, resembling a battery (Freund et al., 2006; Scoville et al., 2015). Thus, the flow of holes generates a current that moves from the stressed area to the unstressed area with electrons becoming trapped at the sites of broken peroxy bonds (Freund et al., 2006).

As holes move from stressed to unstressed regions, at the rock-water interface, they react with water as presented by the reactions in Eqs. (1) and (2) below (Balk et al., 2009; He et al., 2023).



When rocks undergo oxidation,  $O^{\bullet}$  (surface) is produced, which causes the surface of the rock to become hydroxylated. As a result, cations and anions are released from the rock surface into the solution, leading to changes in the groundwater chemistry. Balk et al. (2009) aimed to study the ROS within the  $\equiv SiO^{\bullet}$  matrix of silicates. By subjecting an abraded quartz surface to mechanical forces within an oxygen-depleted environment to simulate conditions deep within the Earth's geology, the researchers observed noticeable concentrations of hydroxyl radicals ( $\bullet OH$ ), superoxide radicals ( $HO_2^{\bullet}$ ), and molecular oxygen ( $O_2$ ). Given their highly oxidative nature, hydrogen peroxide could exhibit a reduced form at water interfaces, particularly in groundwater settings. Freund et al. (2009) and Freund (2010) initially posited that this mechano-chemical generation of reactive oxygen species within groundwater could exert a profound influence during seismic events. The recent study by He et al. (2023) observed the emergence of ROS, with  $H_2O_2$  (97 %) and  $\bullet OH$  (3 %), originating from oxygen-bearing radicals ( $\equiv SiO^{\bullet}$  and  $\equiv SiOO^{\bullet}$ ). The study also estimated the seismic  $H_2O_2$  flux to be  $2.2 \times 10^5 \text{ mol/m}^2 \text{ yr}^{-1}$ . One reported case is Sohna thermal spring water located along the active Sohna fault in Haryana, India, where  $H_2O_2$  concentration has been observed to vary within a range of 0.53 to 0.56 mg/L (Singh & Mukherjee, 2020). Despite a relatively modest augmentation in hydrogen peroxide concentration, its generation could substantially alter the redox chemistry of groundwater, leading to pronounced geochemical transformations. Such mineral–water reactions can potentially initiate a wide range of hydrochemical reactions within the groundwater and cause overflow to the terrestrial surface modifying the chemistry of fresh-water and spring-water. This leads to complex anomalies in groundwater behavior, extensively documented in various studies (Andr n et al., 2016; Biagi et al., 2000; Chen & Wang, 2021; Ide et al., 2020; Kim et al., 2020).

Abnormal variations in ions produced in groundwater could serve as indicators of an impending earthquake. By tracking the temporal and spatial variation of oxidative results and highlighting aberrant variation, successful earthquake warnings may be possible. The presence of organic compounds in groundwater further highlights the importance of studying oxidation at the rock-water interface. The observed changes in fluorescence spectra after an earthquake suggest that the oxidation of organic compounds could also be an indicator of seismic activity. For instance, significant changes in the organic composition of water were observed in fluorescence spectra from a number of samples taken after the massive M5.3 earthquake hit Lago di Garda, Italy on November 24, 2004 (Grant et al., 2011).

The impact of hydrogen peroxide and free radicals on microorganisms can have significant ecological implications. The changes in microbial communities could also be related to the oxidative impact of hydroxyl radicals and other free radicals present in groundwater because of the stress produced prior to and during an earthquake. An example was the L'Aquila Italy earthquake on April 6, 2009, where the number of male toads (*Bufo arenarum*) was seen to decline around the breeding site a few days before the earthquake (Grant & Halliday, 2010). The production of hydrogen peroxide and other oxidants in groundwater could lead to changes in microbial community structure, and in turn, have an impact on nutrient cycling and food webs. For example, the decline of zooplankton and cyanobacteria due to hydrogen peroxide exposure could have ripple effects throughout the food chain, affecting fish populations and potentially causing other ecological disruptions (L rling et al., 2014).

In summary, the production of oxidizing free radicals such as hydroxyl radicals and hydrogen peroxide in groundwater caused by stress produced prior to and during earthquakes can have significant implications for groundwater chemistry and microbial communities.

Understanding the chemistry and biological impacts of these oxidants can provide insight into the mechanisms underlying earthquake warning and the ecological consequences of seismic activity. This article presents evidence that monitoring changes in chemical speciation and microbial activity in groundwater could potentially serve as an early warning system for significant seismic activity. Moreover, this study aims to provide a robust theoretical foundation for understanding the critical and common chemical changes that may occur before an earthquake. Such knowledge can be utilized as one of the parameters in a multifaceted early warning system. A multi-parameter approach is crucial because, although groundwater chemical changes might be linked to seismic events, geological processes are not the sole factors affecting water chemistry. This review further focuses on examining the chemical changes observed following significant seismic activity to identify key changes that might be used predictively as part of a comprehensive multi-parameter tool.

## 2. Aim of the study and literature review

The aim of the review was to address the question: “Can the elevated oxidative potential of hydroxyl radical and hydrogen peroxide generated prior to earthquakes and associated changes be utilized as indicators for earthquake early warning systems?” We compared groundwater chemical precursors reported in previous research (Table 2) with the potential reactions due to  $\bullet OH$  and  $H_2O_2$  listed in Table 1. We conducted a thorough search for papers documenting anomalous hydrogeochemical variations, including ionic changes, and compiled relevant data in Table 2. This included information on earthquake site location, ionic changes preceding the earthquake, pH changes, and temperature changes. We then compared and evaluated the data from Table 2 with the plausible changes in groundwater listed in Table 1 to identify any similarities.

Numerous research studies have been dedicated to forecasting earthquakes using complex and diverse datasets. In this literature review, we employed the PRISMA (Preferred Reporting Items for

**Table 1**

Potential reactions in groundwater developed on the basis of standard reduction potential at the standard condition.

S. N.	Oxidation half-reactions	SRP of Column (I)	Reduction half-reactions	SRP of Column (III)	EMF (V) (Column III-Column I)
1.	H <sub>2</sub> O/H <sub>2</sub> O <sub>2</sub>	-1.35 <sup>b</sup>			
			Ions		
			Na <sup>+</sup> /Na	-2.71	-1.36
			Cl <sub>2</sub> /Cl <sup>-</sup>	1.359	+2.709
			Al <sup>3+</sup> /Al	-1.66	-0.31
			Fe <sup>3+</sup> /Fe <sup>2+</sup>	+0.77	+2.12
			Cu <sup>2+</sup> /Cu	+0.34	+1.69
			CH <sub>4</sub> /HCO <sub>3</sub> <sup>-</sup>	+0.26 <sup>c</sup>	+1.61
			Zn <sup>2+</sup> /Zn	-0.76	+0.59
			K <sup>+</sup> /K	-2.93	-1.58
2.			•O <sup>-</sup> /•OH	1.87 <sup>c</sup>	
	Ions				
	Na(s)/Na <sup>+</sup> (aq)	2.71			-0.84
	Cl <sup>-</sup> /Cl <sub>2</sub>	-1.359			+3.229
	Mg/Mg <sup>2+</sup>	2.37			-0.5
	Al/Al <sup>3+</sup>	1.66			+0.21
	Fe <sup>2+</sup> /Fe <sup>3+</sup>	-0.77			+2.64
	Cu/Cu <sup>2+</sup>	-0.34			+2.21
	Zn/Zn <sup>2+</sup>	0.76			+1.11
	K/K <sup>+</sup>	2.93			-1.06
3.	•OH/H <sub>2</sub> O <sub>2</sub> <sup>d</sup>	-0.39 <sup>b</sup>			
			Ions		
			Na <sup>+</sup> /(aq)/Na (s)	-2.71	-2.32
			Cl <sub>2</sub> /Cl <sup>-</sup>	1.359	+1.749
			Ca <sup>2+</sup> /Ca	-2.87	-2.48
			CH <sub>4</sub> /HCO <sub>3</sub> <sup>-</sup>	0.26 <sup>c</sup>	+0.65
			Mg <sup>2+</sup> /Mg	-2.37	-1.98
			Fe <sup>3+</sup> /Fe <sup>2+</sup>	0.77	+1.16
			Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> /Cr <sup>3+</sup>	1.33	+1.72
			Al <sup>3+</sup> /Al	-1.66	-1.27
4.			•OH, H <sup>+</sup> /H <sub>2</sub> O	2.73 <sup>f</sup>	
	Ions				
	Na(s)/Na <sup>+</sup> (aq)	2.71			+0.02
	Cl <sup>-</sup> /Cl <sub>2</sub>	-1.359			+4.089
	Mg/Mg <sup>2+</sup>	2.37			+0.36
	Al/Al <sup>3+</sup>	1.66			+1.07
	Fe <sup>2+</sup> /Fe <sup>3+</sup>	-0.77			+3.5
	Cu/Cu <sup>2+</sup>	-0.34			+3.07
	Zn/Zn <sup>2+</sup>	0.76			+1.97
	K/K <sup>+</sup>	2.93			-0.2
5.			•HO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> <sup>d</sup>		1.05 <sup>b</sup>
	Ions				
	Na(s)/Na <sup>+</sup> (aq)	2.71			-1.66
	Cl <sup>-</sup> /Cl <sub>2</sub>	-1.359			+2.409
	Mg/Mg <sup>2+</sup>	2.37			-1.32
	Al/Al <sup>3+</sup>	1.66			-0.61
	Fe <sup>2+</sup> /Fe <sup>3+</sup>	-0.77			+1.82
	Cu/Cu <sup>2+</sup>	-0.34			+1.39
	Zn/Zn <sup>2+</sup>	0.76			+0.29
	K/K <sup>+</sup>	2.93			-1.88
6.			H <sub>2</sub> O <sub>2</sub> /H <sub>2</sub> O		1.35 <sup>b</sup>
	Ions				
	Na(s)/Na <sup>+</sup> (aq)	2.71			-1.36
	Cl <sup>-</sup> /Cl <sub>2</sub>	-1.359			+2.709
	Mg/Mg <sup>2+</sup>	2.37			-1.02
	Al/Al <sup>3+</sup>	1.66			-0.31
	Fe <sup>2+</sup> /Fe <sup>3+</sup>	-0.77			+2.12
	Cu/Cu <sup>2+</sup>	-0.34			+1.69
	Zn/Zn <sup>2+</sup>	0.76			+0.59
	K/K <sup>+</sup>	2.93			-1.58

Sources: <sup>b</sup>(Koppenol et al., 2010); <sup>c</sup>(Palmisano & Hazen, 2003); <sup>d</sup>(Balk et al., 2009); <sup>e</sup>(Wardman, 1989); <sup>f</sup>(Habashi, 1993).

Systematic Reviews and Meta-Analyses) method to explore the literature on changes in groundwater geochemistry for earthquake warning. The application of PRISMA principles is as follows:

We conducted a keyword search on the Scopus database using the following search terms: Earthquake\* AND (“precursor\*” OR “Prior” OR “before” OR “pre-earthquake” OR “Pre-seismic” OR “earl\*” OR

“Preced\*”) AND (“Hydrochemi\*” OR “Hydrogeochemi\*” OR “Concentration\*” OR “Content\*” OR “Chemi\*” OR “Ionic” OR “Ions” OR “Ion”) AND Groundwater\* AND (“Observ\*” OR “data” OR “sample\*” OR “borehole\*” OR “record\*” OR “result\*” OR “well\*”) for title-abstract and keywords. This search returned 315 papers published up until 14 January 2024 in this field.

The literature analysis of ionic data for certain earthquakes was the main focus of PRISMA. To ensure the relevance of the obtained papers, we first screened them based on their titles. Out of 335 articles, 157 were left after the initial screening, and the majority of them dealt with the total electron content (TEC), which was not the subject of our review. After elimination, 99 papers remained for further assessment. 14 of the 99 papers were written in other languages, and 17 papers were still outside the scope of the review. The remaining papers provided insights on gas anomalies and isotopic variations, which were included for qualitative analysis, in addition to the ionic alterations in groundwater. After the four phases of screening (Fig. 1), 49 papers were selected for a detailed qualitative review of 32 various earthquakes which are summarized in Table 2. To analyze ionic anomalies for exclusive earthquakes, PRISMA was adopted.

The literature review in groundwater chemistry revealed four primary themes: 1) The changes in ionic chemistry, assessed through electrode potential data; 2) Processes occurring at mineral surfaces in response to peroxide and radicals; 3) The oxidation of organic molecules; 4) The effect on microorganisms, including zooplankton, phytoplankton, bacteria, and archaea, observed before and immediately after earthquakes. Fig. 2 below provides a visual representation of the interconnection of these major themes. The fundamental science and generation mechanism of h<sup>•</sup>, •OH, H<sub>2</sub>O<sub>2</sub> in Fig. 2 were already discussed in the introduction section.

### 3. Findings from previous studies of the earthquake precursors

The following section presents the results of our review of the relationship between earthquakes and groundwater chemistry. The section is structured into four parts, representing the four major themes identified in the PRISMA approach.

#### 3.1. Changes in ionic chemistry (Theme 1)

Groundwater chemistry is predominantly influenced by ionic species. Investigating the impact of hydroxyl radical and hydrogen peroxide on these ions could offer valuable insights into potential changes in groundwater where oxidizing species are present. Previous studies have examined changes in groundwater ionic composition prior to earthquakes (Andrén et al., 2016; Barberio et al., 2017; Malakootian & Nouri, 2010; Skelton et al., 2008). Most of them include the ionic anomalies for earthquakes with a magnitude above five (M>5.0). This can be related to the stress accumulated in rock prior to an earthquake. These studies suggest that pre-earthquake variations are mainly caused by mineral dissolution, dilution, volume replacements, and groundwater mixing from fractures, silts, or strains, both stoichiometric and non-stoichiometric. However, little research has been conducted on the connection between these ionic changes and •OH and H<sub>2</sub>O<sub>2</sub>.

As ionic species tend to dominate groundwater chemistry, the study of the implication of hydroxyl radical and hydrogen peroxide on these ions might provide important insight into potential changes in groundwater where these oxidizing species are present. The majority of studies contend that precursory variations are caused by stoichiometric and non-stoichiometric mineral dissolution, dilution, volume replacements, and groundwater mixing from fractures, silts, or strains. The connection of these ionic changes to •OH and H<sub>2</sub>O<sub>2</sub> has hardly been studied.

Groundwater typically contains dissolved inorganic ions and organic compounds, which can undergo oxidation when peroxide is present. Assessing the spontaneity of these reactions in groundwater involves considering the electrochemical series and standard reduction potentials

**Table 2**

Overview of past studied earthquake chemical precursors before the earthquakes.

References	Name of the earthquake	Geographic zone	Geological settings (faults, minerals & rocks)	Changes in groundwater quality parameters	
				Trace Elements/Ions	pH, temperature, Organics
(Favara et al., 2001)	<sup>a</sup> M5.6 and M5.3 Belice Valley Earthquakes 1985	Monteyag Western Sicily	Sedimentary basins: Limestone, Gypsum, Halite, Kainite, Sylvite	Dissolved SO <sub>4</sub> <sup>2-</sup> , Cl, Na and TDS increase	Carbonate and selenite waters, temperature increase
(Biagi et al., 2004; Biagi et al., 2006; Kingsley et al., 2001; Kopylova & Boldina, 2019)	Kamchatka March 2, 1992 1 January 19, 1965 December 1997	Kamchatka Peninsula	Soft Quaternary Deposits, Obligocene, Miocene Rocks	Increase in SO <sub>4</sub> <sup>2-</sup> , Na <sup>+</sup> , Ca <sup>2+</sup> after quake Sharp Decrease in Cl <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> 3–5 months prior	Before the 1992 earthquake, nitrogen, and argon gas increased, and deep-seated gases, methane, helium, and carbon dioxide decreased
(Shimizu et al., 1996)	M4.0 Kamaishi Earthquake 1993	North of Tokyo, Japan	Granodiorite, Monzonites, Diorites	Increase in Na <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup>	–
(Hartmann & Levy, 2006; Tsunogai & Wakita, 1995)	M7.2 Hyogoken-Nanbu Earthquake 1995	Kobe, Japan	Granitic (Granitic Rokko Mountains)	Increase: Cl <sup>-</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup> , Sr <sup>2+</sup> Decrease: Na <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup>	Increase in Radon Concentration
(Yechieli & Bein, 2002)	M7.1 Nuweiba Earthquake 22 November 1995	Dead Sea Rift Valley	Sedimentary Rocks of Cretaceous to Tertiary age	Increase in Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup>	Well level increased
(Pérez et al., 2008)	M4.6 Lugo Earthquake 29 November 24 December 1995	Galicia, Spain	–	Increase in dissolved Cl <sup>-</sup> , CO <sub>2</sub> three months prior	NaHCO <sub>3</sub> type groundwater Radon Activity
(Toutain et al., 1997)	M5.2 Pyrenean earthquake Feb 18, 1996	Boundary France and Spain	Carbonate Karstic Limestones and dolomite	Increase in Ca <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> Decrease in HCO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup>	High HCO <sub>3</sub> <sup>-</sup> concentration: Interaction with carbonate rocks
(Federico et al., 2004)	M3.6 Vesuvius Earthquake 9 Oct 1999	Vesuvius, Italy	–	Increase and decrease in different wells Ca <sup>2+</sup>	pH changes according to increase and decrease of ions noted, temperature variations
(Balderer et al., 2002)	M7.6 Izmit Earthquake 17 August 1999	Northwest Turkey	North Anotolian Fault Zone	Increase and decrease (wells) Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup>	<sup>13</sup> C content of TDIC variation, pH 6.6–7.6
(Song et al., 2006; Song & Ku, 2003)	M7.3 Chi-Chi Earthquake 21 September 1999	Kuantzeling West-Central Taiwan	Chelungpu Tertiary Folds and faults	Increase in Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup>	Increased Groundwater level
(Zhou et al., 2022)	M6.0 Dayao Earthquake 21 July 2003	Yunnan China	Lanping-Simao Fault Basin	Increase in Ca <sup>2+</sup> , Mg <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup>	No approximate Groundwater change
(Malakootian & Nouri, 2010)	M6.5 Bam Earthquake 26 Dec 2003	Southeast Iran	–	Increase trend of SO <sub>4</sub> <sup>2-</sup> , Na <sup>+</sup> , Cl <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	Sudden increase in electrical conductivity and TDS following decrement
(Reddy et al., 2017)	M5.1 14 March 2005	Koyna and Warna Reservoirs India	Deccan Volcanic Province	Increase in F <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	Decrease in δ <sup>18</sup> C Ground water type: Ca- HCO <sub>3</sub> , Ca-Na- HCO <sub>3</sub> , Na- HCO <sub>3</sub> - CO <sub>3</sub>
(Zhou et al., 2022)	M6.1 Ning'er Earthquake 2 June 2007	Yunnan China	Lanping-Simao Fault Basin	Increase in Ca <sup>2+</sup> , Mg <sup>2+</sup> Decrease in HCO <sub>3</sub> <sup>-</sup>	Groundwater discharge increase
(Keskin, 2010)	M3.2 Karabuk Earthquake 28 September 2007	Turkey	Lacustrine Limestone, Basalt, Shale, Calcareenite, Sandstone, Conglomerate	Decrease in Na <sup>+</sup> , Ca <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup>	EC <sup>a</sup> decreased, Groundwater type: Mg, Ca, Na-HCO <sub>3</sub>
(Inan et al., 2010)	M4.2 Turkey Earthquake 10 Jan, M4.7 Turkey Earthquake 200, 825 April 2008	Western Turkey	Metamorphic Paleozoic Age. Pliocene to Quaternary Limestones and silico-clastic rocks	Increase in Ca <sup>2+</sup> , Mg <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> Decrease in Na <sup>+</sup>	<sup>b</sup> EC increased
(Li et al., 2019; Yan et al., 2022)	M8.0 Wenchuan Earthquake 2008	Western China	Xianshuihe Fault Siltstone, Quartz, Sandstone, Mudstone, Slate, Granite, Diorite	Decrease in Na <sup>+</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> after quake	pH: 6.25–9.45 and HCO <sub>3</sub> -Cl-Na HCO <sub>3</sub> -Ca-Na HCO <sub>3</sub> -Na-Mg
(Falcone et al., 2012)	M6.3 L'Aquila Earthquake 6 April 2009	L'Aquila, Italy	Triassic Dolomites, Jurassic Cretaceous, Meso-Cenozoic carbonate rocks	Increase in Ca <sup>2+</sup> , Mg <sup>2+</sup> Post trend: Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	Higher pH in pre-seismic period
(Kaihotsu et al., 2017)	M9.0 Tohoku Earthquake, 2011	Japan	–	Increase in Na <sup>+</sup> , Ca <sup>2+</sup> , Cl <sup>-</sup> after earthquake	High electric conductivity, all might be due to Tsunami
(Andrén et al., 2016; Skelton et al., 2014)	M5.6 Earthquake 2012 M5.3 Earthquake 2013	Iceland (Borehole: Husavik and Hafraalekur)	Zeolite, Plagioclase, Pyroxene, Breccia	Increase in concentration of Si, Na <sup>+</sup> , Ca <sup>2+</sup> , δ <sup>2</sup> H, δ <sup>18</sup> O	Average pH of 10.3
(Li et al., 2019; Yan et al., 2022)	M7.0 Lushan Earthquake 2013	Western China	Xianshuihe Fault Siltstone, Quartz, Sandstone, Mudstone, Slate, Granite, Diorite	Increase in Na <sup>+</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	pH: 6.25–9.45 Groundwater type: HCO <sub>3</sub> -Cl-Na HCO <sub>3</sub> -Ca-Na HCO <sub>3</sub> -Ca-Na HCO <sub>3</sub> -Na-Mg
(Chen & Wang, 2021)	M6.1 Yingjiang Earthquake 30 May 2014	Ganze Spring	Quaternary Lacustrine and alluvium: Sandstone and Mudstone	Decrease: Ca <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> , Mg <sup>2+</sup> after quake slight increase in HCO <sub>3</sub> <sup>-</sup> prior	Decrease due to dissolution of karst system

(continued on next page)



Table 2 (continued)

References	Name of the earthquake	Geographic zone	Geological settings (faults, minerals & rocks)	Changes in groundwater quality parameters	
				Trace Elements/Ions	pH, temperature, Organics
(Zhou et al., 2022)	Jinggu Earthquake M6.1–7 OctoberM5.6–5 December 2014	Yunnan, China	Lanping-Simao Fault Basin	Decrease in $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{HCO}_3^-$	No approximate groundwater change
(Li et al., 2019; Yan et al., 2022)	M6.3 Kangding Earthquake	Western China	Xianshuihe FaultSiltstone, Quartz, Sandstone, Mudstone, Slate, Granite, Diorite	Increase in $\text{Na}^+$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ two months before the quake	pH: 6.25–9.45Groundwater type: $\text{HCO}_3\text{-Cl-Na}$ $\text{HCO}_3\text{-Ca-Na}$ $\text{HCO}_3\text{-Ca-Na}$ $\text{HCO}_3\text{-Ca-Na}$ $\text{HCO}_3\text{-NaMg}$
(Koizumi et al., 1996; Sato et al., 2020)	M7.0 Kumamoto Earthquake April 16, 2016	Kyushu Island (Southern Japan)	Pre-Aso Volcanic Rock, Paleozoic and Mesozoic Rock	Drop in $\text{Mg}^{2+}$ , Increase in $\text{NO}_3^-$ after earthquake $\text{Na}^+$ , $\text{K}^+$ $\text{Cl}^-$ , $\text{SO}_4^{2-}$	Spring water
(Zhou et al., 2022)	M5.1 Yangbi EarthquakeMarch 27, 2017	Yunnan, China	Rhombic RocksCarbonatite, Silicate and Gypsum	South increase in $\text{Na}^+$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ North decrease in $\text{Na}^+$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ Increase: $\text{Ca}^{2+}$ , $\text{HCO}_3^-$	$\text{SO}_4\text{Cl-NaCa}$ , $\text{Cl-NaCa}$ , $\text{HCO}_3\text{SO}_4\text{-Na}$ type springs
(Li et al., 2022)	M5.7 Mojiang 8 September 2018	Yunnan, China	Lanping-Simao BasinTriassic carbonate rocks	Increase in $\text{Ca}^{2+}$ , $\text{Na}^+$ , $\text{HCO}_3^-$ one month before the earthquake	Changing groundwater due to the increase in $\text{Ca}^{2+}$ , $\text{HCO}_3^-$
(Gori & Barberio, 2022)	M3.9 San Leucio del Sannio Earthquake 16 Dec 2019	Grassano Spring, Italy	Meso-Cenozoic Carbonate, Limestone, dolomitic limestone	Increase in $\text{Ca}^{2+}$ , $\text{Na}^+$ , $\text{HCO}_3^-$ one month before the earthquake	Increase in $\text{CO}_2$
(Wang et al., 2021)	M6.1 Hualien Earthquake 18 April 2021	Taiwan	Tertiary- Quaternary Terrestrial Sedimentary Strata	Increase in $\text{Na}^+$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ before 85–168 days	TDS increase
(Luque-Espinar & Mateos, 2023)	2020–2021 seismic sequence	Granada (S Spain)	Internal-Alpine metamorphic rocks, External –sedimentary-mesozoic and tertiary-rocks, Hongyanchi thrust fault, gypsum and kaolin	$\text{HCO}_3^-$ decrease, $\text{Cl}^-$ and $\text{SO}_4^{2-}$ increase, $\text{Ca}^{++}$ and $\text{Mg}^{++}$ increase	pH and temperature decrease
(Xiang & Peng, 2023)	Xinjiang earthquake 8 Dec 2018	Xinjiang (China)		Slight increase in $\text{SO}_4^{2-}$ , $\text{Cl}^-$ , $\text{Na}^+$ , $\text{Mg}^{++}$ , $\text{Ca}^{++}$ , $\text{K}^+$ before earthquake and abrupt decrease after earthquake	
(Zhou & Zhong, 2022)	M4.8 Urumqi earthquake 12 Dec 2020	Urumqi (China)	North Tianshan Mountain of northwestern China, Permian oil shale and siliceous sandstone	Slight increase in $\text{SO}_4^{2-}$ , $\text{Cl}^-$ , $\text{Na}^+$ , $\text{Mg}^{++}$ , $\text{Ca}^{++}$ , $\text{K}^+$ before earthquake.	

<sup>a</sup> M5.6 stands for the magnitude of 5.6., <sup>b</sup> EC stands for Electrical Conductivity.

(SRP). By utilizing this information, it becomes possible to estimate the free energy and spontaneity of processes taking place in the groundwater using the electromotive force (EMF) (Hamilton, 2000; Vanysek, 2000). Previous studies have identified the most likely processes and reactions in groundwater based on the standard reduction potentials summarized in Table 1 (Balk et al., 2009; Freund, 2010; Freund et al., 2006; Scoville et al., 2015; Koppenol et al., 2010; Palmisano & Hazen, 2003; Wardman, 1989). Table 1 is useful because those processes with an overall positive EMF are likely to be those that are spontaneous in groundwater systems. Table 1 shows that  $\text{Na}^+$ ,  $\text{Al}^{3+}$ , and  $\text{K}^+$  are not likely to be reduced during the oxidation of water into hydrogen peroxide, while  $\text{Al}$ ,  $\text{Cu}$ ,  $\text{Zn}$ , and  $\text{Fe}/\text{Fe}^{2+}$  are readily oxidized to  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Fe}^{3+}$ , respectively, with the generated holes being reduced to hydroxyl radicals. Table 2 indicates that many earthquakes exhibit changes in the speciation of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Fe}^{2+}$ , and  $\text{Cu}^{2+}$  ions, in line with the speciation reactions described in Table 1.

Fig. 3 illustrates the variations in the speciation and concentration of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{2-}$  ions during 32 earthquakes. The data reveal that  $\text{Cl}^-$  ions exhibit the highest variance, followed by  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{Mg}^{2+}$ . However, the explanation for the release of Sulphur ions is provided in Section 3.2. The reported data shows that concentrations increase more than they decrease.

The data reveals that prior to earthquakes, significant ionic changes occur in  $\text{Na}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Ca}^{2+}$  in groundwater due to exposure to hydrogen peroxide and hydroxyl radicals. These anomalies can be useful for earthquake early warning systems, especially for earthquakes with magnitude (M) greater than five ( $M > 5.0$ ) as a higher magnitude can

imply higher stress accumulation, and higher stress can result in elevated generation of holes and electrons (Freund, 2010). This can in turn generate more hydrogen peroxide, thus changing the ionic concentrations in groundwater. In Northern Ireland, after the 2002 earthquake, variances in species such as Ba, Li, Mo, Rb, Si, and Sr were recorded in groundwater (Malakootian & Nouri, 2010). The 5.4 magnitude Kraljevo earthquake in 2010 showed a significant increase in Al and heavy metals (Cu, As, Pb, Zn, and Cr) as pre-seismic and post-seismic signals (Jakovljević & Lozanov-Crvenković, 2015). Additionally, (Martinelli et al., 2017) reported fluctuations and an increase in chloride and bicarbonate concentrations after the M5.9 Po Valley earthquake in 2012.

3.2. Processes at mineral surfaces involving  $\text{H}_2\text{O}_2$  and  $\bullet\text{OH}$  (Theme 2)

Groundwater typically comes into contact with various mineral phases and rock surfaces, leading to redox processes at these surfaces. Because of the scarcity of data on SRP for rock compounds, this review was constrained to prior research that examined alterations in minerals in the presence of hydroxyl radicals and hydrogen peroxide. Table 3 displays common oxidative, hydrolysis, and dissolution reactions that occur under normal conditions. Examining changes in speciation in the presence of hydrogen peroxide and hydroxyl radicals may enable the identification of indicator species that could potentially indicate the presence of peroxide and radicals in groundwater.

A good example of the importance of these surface processes is the oxidation of iron pyrites (Jennings et al., 2000) in the presence of

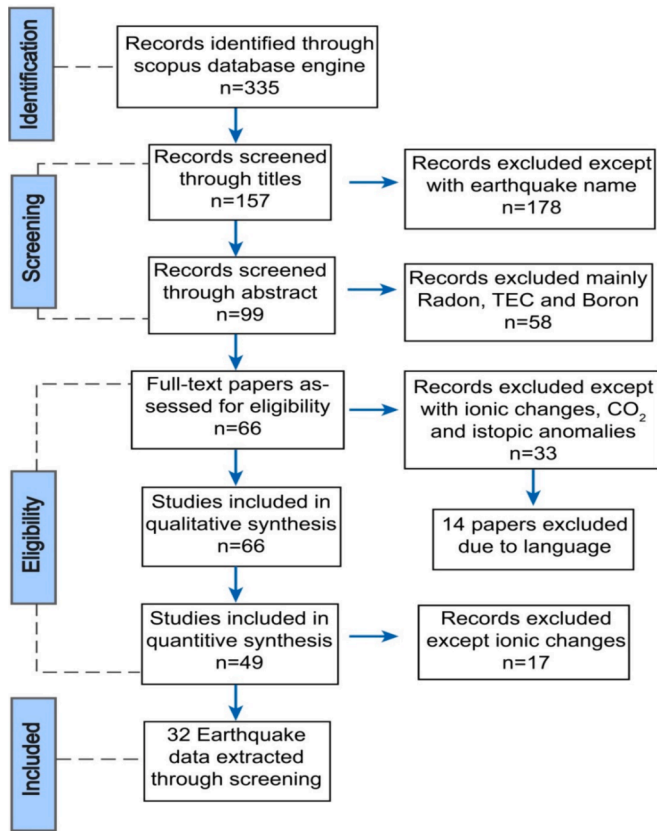


Fig. 1. Screening steps using PRISMA for systematic review and analysis of earthquake precursors from the Scopus database.

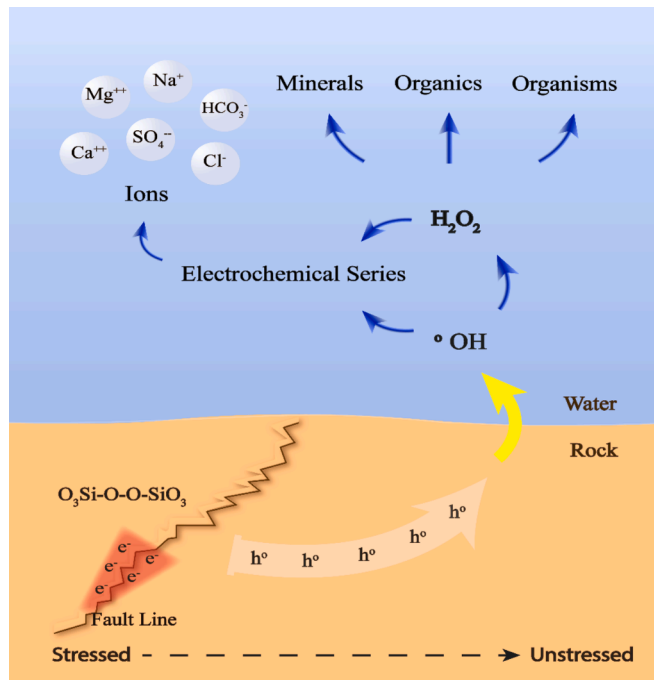
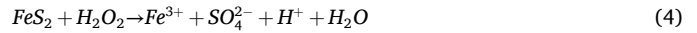
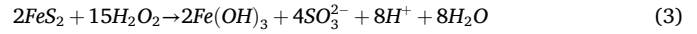


Fig. 2. The formation of hydrogen peroxide from short-lived hydroxyl radical at the rock-water interface and the response of the groundwater constituents: Ions, minerals, organics, and organisms to the hydrogen peroxide.

hydrogen peroxide Eqs. (3) and (4).



The reactions above confirm the production of ferric hydroxide and sulfate ions as a result of pyrite oxidation in the presence of hydrogen peroxide. At low temperatures and pH, the hydroxide is unstable, and thus, ferric ions are formed instead (Jennings et al., 2000; Mckibben & Barnh, 1986). The reaction also emphasizes the release of sulfate ions into groundwater, which is reflected in the earthquake data presented in Table 2.

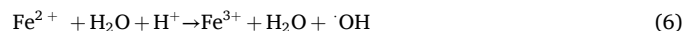
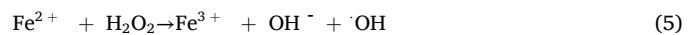
Hydrogen peroxide present in groundwater can be decomposed by iron oxides, iron-containing minerals such as ferrihydrite, goethite, iron-containing clays, and iron-coated sand, creating a potent oxidant that can oxidize various contaminants. Manganese oxides such as birnessite and pyrolusite are highly effective in catalyzing  $\text{H}_2\text{O}_2$  decomposition as well (Pham et al., 2012).

Notably, soil in the vicinity of vanadium titanomagnetite mining sites often contains high levels of vanadium (V) alongside other organic pollutants such as diethyl phthalate (DEP), which are frequently detected in soil and groundwater. It has been discovered that vanadium minerals can accelerate  $\text{H}_2\text{O}_2$  decomposition in groundwater to produce  $\bullet\text{OH}$  for the degradation of DEP in both soil slurry and aqueous solutions over a wide pH range. Furthermore, similar to the cycles of  $\text{Fe}(\text{II})/\text{Fe}(\text{III})$  (0.77 V) in the  $\text{Fe}$ -mineral/ $\text{H}_2\text{O}_2$  system, the cycles of  $\text{V}(\text{IV})/\text{V}(\text{V})$  by  $\text{H}_2\text{O}_2$  are thermodynamically feasible due to their comparable reduction potential (0.99 V) (Fang et al., 2018).

### 3.3. Oxidation of organic molecules (Theme 3)

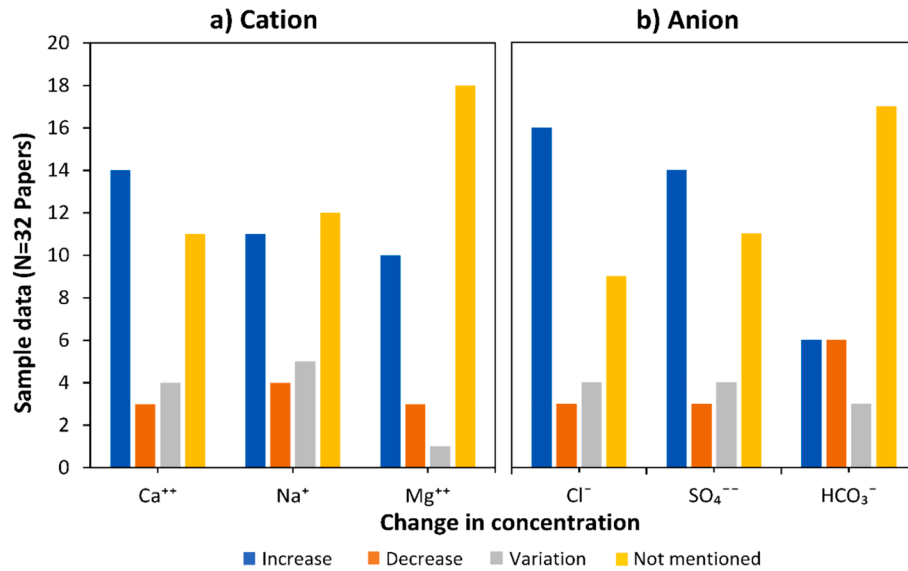
Changes to the composition of organic species in water can be brought about by oxidizing agents, especially the presence of species such as hydroxyl radical and hydrogen peroxide where processes analogous to the Advanced Oxidation Process (AOP) can occur. Such processes have been observed in groundwater systems (Kwan & Voelker, 2003). AOP is a chemical treatment technique used to degrade and remove various pollutants from water and wastewater. It involves the generation of highly reactive hydroxyl radicals ( $\bullet\text{OH}$ ) or other powerful oxidizing agents to break down and transform organic and inorganic contaminants into less harmful substances. AOPs are effective in treating a wide range of pollutants, including organic compounds, pesticides, pharmaceuticals, industrial chemicals, and even certain pathogens (Kanakaraju et al., 2018; Oturan & Aaron, 2014; Paudel et al., 2018).

The Fenton Process, Photo-assisted Fenton Process, and UV/peroxide oxidation are some of the well-known AOP methods. As with wastewater treatment, the groundwater chemistry is a crucial factor in AOP. The oxidation of organic substances can be achieved through the Fenton Process (Oturan & Aaron, 2014) which utilizes ferrous and ferric ions. This process takes place in mildly acidic conditions in the presence of hydrogen peroxide. The reaction involved in this process can be represented by Eqs. (5) and (6). In addition, both equations also support the potential change in groundwater brought on by the ferrous ions.



Hydroxyl radicals produced can then oxidize organic compounds present in the water in ways presented in the generalised Eqs. (7), (8), and (9) (Kanakaraju et al., 2018).





**Fig. 3.** a) Cationic concentration changes were observed from a data set of N=32 papers, b) Anionic concentration changes were observed from a data set of N=32 papers. Increase, decrease, variation, and not mentioned indicate the changes in the ionic concentration.

**Table 3**

Rock-water interface reactions through different chemical weathering processes under normal conditions (Elango & Kannan, 2007).

Mineral	Chemical Formula	Relative Resistance	Chemical Weathering Process
Pyrite	FeS <sub>2</sub>	Low	Dissolution and oxidation
Olivine	(Fe, Mg)SiO <sub>4</sub>	Moderately low	Oxidation and Hydrolysis
Pyroxene	Ca, Fe, Al, Mg silicates	Moderate	Oxidation and Hydrolysis
Hornblende (Amphibole)	Na, Ca, Fe, Al silicates	Moderate	Oxidation and Hydrolysis
Biotite	K, Fe, Mg, Al silicates	Moderate	Oxidation and Hydrolysis



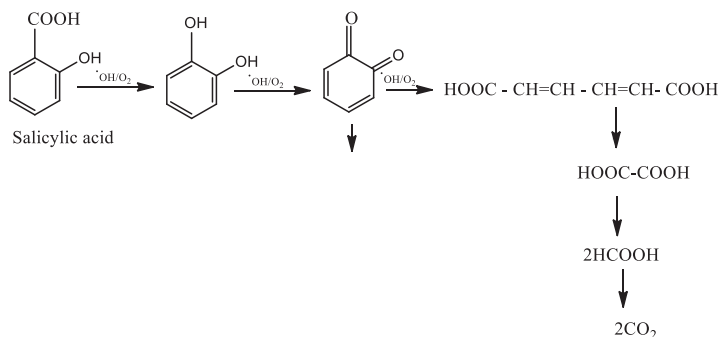
The Fenton Process, AOP, and ferric ions have the capability to oxidize organic compounds and microorganisms. However, groundwater lacks UV radiation, which is typically involved in the oxidation process. Instead, electromagnetic radiation has been observed as a precursor to earthquakes (Akhoondzadeh et al., 2010; Bleier et al., 2010; Qian et al., 1996; Ohta et al., 2001; Parrot et al., 1993; Petraki et al., 2015) that is generated in stressed rock at fracture joints. Prior to earthquakes, positive holes are generated in the mineral phase and can rapidly spread and penetrate surrounding rock, inducing currents of hundreds of millions of amperes in the Earth's crust. These currents create electromagnetic radiation as they fluctuate, with ultra-low frequency electromagnetic waves traveling through tens of kilometers of rock and being detectable at the Earth's surface (Bortnik et al., 2010). In addition, infrared emissions can be detected by seismo-electromagnetic satellites. Therefore, although we can eliminate oxidative damage to organic molecules that relies on UV radiation, we must also recognize that there may be other forms of radiation at different wavelengths that can provide the activation energy required to initiate the oxidation process.

At ambient temperature and pressure, AOP generates highly reactive radicals, particularly hydroxyl radicals, which can destroy organic pollutants through oxidation. Hydroxyl radicals are non-selective and extremely reactive oxidizing entities because of their high oxidation potential, allowing them to react with most organic compounds. As a result of their non-selective nature, hydroxyl radicals can easily remove

or damage various vulnerable organic chemical compounds such as acids, alcohols, aldehydes, aromatics, amines, ethers, ketones, and so on (Sievers, 2011).

AOP can effectively destroy a wide range of pollutants, including detergents, pesticides, nitrophenols, halogenated hydrocarbons (such as trichloroethane and trichloroethylene), aromatic compounds (such as benzene, toluene, ethylbenzene, xylene – BTEX), Pentachlorophenol (PCP), chlorobenzene (Dilmeghani & Zahir, 2001), and other dissolved organic contaminants (Liu et al., 2017; Tiburtius et al., 2005). In groundwater with high carbonate alkalinity, which is typical, organic substrates must compete with natural organic matter, hydrogen peroxide, bicarbonate, and carbonate ions for reactivity with the hydroxyl radical (Glaze et al., 1995). AOPs have the potential to oxidize both organic and inorganic contaminants, including sulfur, nitrite, and cyanide. The rate of degradation of the contaminants is dependent on their rate constant with hydroxyl radicals. Chlorinated organic molecules are first transformed into intermediates such as aldehydes and carboxylic acids, then converted into CO<sub>2</sub>, H<sub>2</sub>O, and Cl<sup>-</sup> ions. Inorganic contaminants are oxidized to sulfate, nitrate, or free N<sub>2</sub>, and cyanide is transformed into cyanate, which is further processed to produce CO<sub>2</sub> and NO<sub>3</sub> (or N<sub>2</sub>) (Sievers, 2011). Compounds containing carbon are oxidized to carbon dioxide, while elements bound to organic compounds are transformed into anions such as nitrates, sulfates, or chlorides (Kaur et al., 2019).

Some organic compounds easily discovered in groundwater include sulfathiazole (STZ), sulfamethoxazole (SMZ), and sulfamethazine (SMT). These molecules can easily and swiftly spread across the environment since they are highly migratory, polar, amphoteric, water-soluble compounds with light and heat stability. The oxidative degradation of sulfonamides causes an increase in the H<sub>2</sub>O<sub>2</sub> concentration since it would improve energy harvesting and hydroxyl radical production. In addition, the toxicity of sulfonamides gradually reduces as the reaction progresses (Zhu et al., 2019). The typical building blocks of aquatic humic matter are the organic chemicals phenol, salicylic acid, and vanillic acid. Aliphatic diacids were the primary intermediates produced by advanced oxidation processes (AOPs), which are subsequently transformed into two molecules of formic acid and then oxidized by hydroxyl radicals to produce carbon dioxide. Eq. (10) shows oxidation of Salicylic acid by hydroxyl radical (Gligorovski et al., 2015).



(10)

(10)

Because of the defect in rocks, an oxidation reaction occurs, and organics may partly oxidized to volatile ketones, aldehydes, and acids and finally to gases like carbon monoxide (CO) (Grant et al., 2015). There is plenty of evidence that earthquakes release different gases from deep within the earth's mantle. These gases could include non-biological methane, which could be a massive source of fuel. Under high pressure and temperature conditions, the hydrocarbons would release methane as the primary mobile component (American et al., 1980). In addition, Helium and Argon are highly mobile, conservative species accumulated in rocks, liberated from mineral grains as the rock deforms. They could be utilized to provide information on changes in the state of stress and strain in earth materials (Bauer et al., 2016). In summary, besides carbon dioxide, toxic gases like carbon monoxide and other trace gases such as hydrogen, nitrogen, helium, argon, and methane are frequently emitted, with isotopic evidence pointing to an upper mantle (Freund & Stolz, 2013; Kaur et al., 2019).

These observations support significant gas emissions and trace gas emissions that are associated with seismic activities (Gori & Barberio, 2022; Kopylova & Boldina, 2021; Pérez et al., 2008). Moreover, the reactions involved during the oxidation of the organic compounds can aid in explaining the increased concentration of chlorides and sulphates associated with seismic events (Li et al., 2019; Sato et al., 2020; Yan et al., 2022; Zhou et al., 2022). This evidence suggests that the potential reactivity of hydroxyl radicals with organic molecules in groundwater may be responsible for the gaseous and some ionic anomalies.

### 3.4. Effect of hydrogen radical and hydrogen peroxide on microorganisms (Theme 4)

Changes in water chemistry play a significant role in shaping microorganisms and biology. Water chemistry encompasses various physical and chemical parameters such as pH, temperature, dissolved oxygen, nutrient concentrations, salinity, and the presence of contaminants or pollutants. Modifying these factors can directly or indirectly impact microorganisms and biological processes within aquatic ecosystems. While a considerable amount of literature exists documenting these influences, there is a relative lack of studies specifically investigating groundwater systems and examining the direct consequences of changes in groundwater chemistry on aquatic organisms. Consequently, it becomes necessary to explore literature that may not directly focus on groundwater but examines the impact of speciation changes, which are likely to occur in groundwater systems prior to an earthquake.

Studies have examined the potential effects of hydroxyl radicals and hydrogen peroxide on aquatic organisms such as zooplankton, phytoplankton, bacteria, and crustaceans (Bailey et al., 2018; Burson et al., 2014; Grant & Conlan, 2015; Kim et al., 2020; Lüring et al., 2014; Matthijs et al., 2012; Reichwaldt et al., 2012; Zhang et al., 2006). While some microorganisms have shown less tolerance to hydrogen peroxide (Lusty & Gobler, 2020; Piel et al., 2021; Schmidt et al., 2006; Spoof

et al., 2020), others have demonstrated adaptive behavior to resist damage caused by it. However, changes in behavior have been observed in certain algae, fish, invertebrates, and larvae of euphausiids and oysters when exposed to hydrogen peroxide. Several studies have also evaluated the use of hydrogen peroxide as a potential algicide in freshwater aquaculture. Algae such as *Raphidiopsis* spp. (Dziga et al., 2019), *Microcystis* spp. (Huo et al., 2015; Papadimitriou et al., 2022; Schmidt et al., 2006), zoo-plankton like *Calanus* spp. (Escobar-Lux et al., 2020), and phytoplankton such as *Chrysochromulina* spp. (Schmidt et al., 2006) are potentially impacted by exposure to hydrogen peroxide in freshwater and brackish water. Fish such as Walleye (*Sander vitreum*) (Rach et al., 2003), invertebrate *Gammarus* spp (Escobar-Lux et al., 2020), zebra mussels *Dreissena polymorpha*, larvae of a euphausiid *Euphausia pacifica*, and an oyster *Crassostrea gigas* (Jo et al., 2008) have shown significant behavioral changes (Schmidt et al., 2006).

Studies conducted by (Drábková et al., 2007) and (Jiang et al., 2022), investigated the potential use of hydrogen peroxide as an algicide in freshwater aquaculture. However, despite anaerobic bacteria being the least tolerant to hydrogen peroxide, it has been suggested that bacteria are not the most sensitive aquatic species (Schmidt et al., 2006). This is because of their adaptive behavior, which allows them to resist damage caused by peroxide, which has been demonstrated in several studies. For instance, research on *Vibrio harveyi* (Vattanaviboon et al., 2003), *Edwardsiella tarda* in fish (Bera et al., 2020), *Pseudomonas syringae* (Brown et al., 1995), and biofilm-forming bacteria (Armon et al., 2000) have shown that these organisms adapt by activating the catalase gene. This gene produces an enzyme that breaks down peroxide, thereby protecting the bacteria from its harmful effects. However, Drábková et al. (2007) demonstrated that hydrogen peroxide has a comparatively greater effect on cyanobacteria than green algae. To further investigate the behavioural modifications, previous data on the behavior of microorganisms before an earthquake was analyzed to understand the alterations in their behavior in response to hydrogen peroxide exposure. These changes were then confirmed using the pre-existing observations.

In this review, we found 11 studies that investigated microbiology before and after earthquakes, all of which showed differences. Table 4 summarizes the changes in organisms associated with an earthquake, with studies examining the prior and post-seismic responses on groundwater ecology and habitat changes. Some changes may be caused by sediment redistribution, while others are likely because of chemistry changes in the groundwater which might alter the availability of nutrients as well. Four of these studies attributed to the observed changes in oxidative stress caused by hydrogen peroxide. *Daphnia logispina* was observed to be affected during the 1966 earthquake at Lake Sevan, where a decrease in zooplankton biomass was also noted, as they are less tolerant to hydrogen peroxide. Similarly, a significant decrease in the cyst *Alexandrium* was observed from August 2011 to May 2012 during the Great East Japan Earthquake (Natsuike et al., 2014), which could be the result of the termination of the *Alexandrium* bloom by hydrogen



**Table 4**  
Implications of groundwater chemistry and behavior change of organisms before earthquakes.

References	Name of Earthquakes	Country/Region	Changes in organisms' behavior	Cross-validated parameters
(Brancelj, 2000, 2021; Radziminovich et al., 2010)	Lake Baikal August 1912	South Baikal	Released a large amount of methane into the water column mass-killed Baikal oil fish ( <i>Comephorusbaikalensis</i> )( <i>C. dybowskii</i> )	
(Wang et al., 2006)	M7.3 Haicheng earthquake, February 04, 1975	Northern China	Hundreds of snakes coming out of hibernation in subzero temperatures	
(Ikeya et al., 2000; Grant et al., 2011)	M7.2 Kobe earthquake, 1995	Japan	<i>Trachipterus ishikawae</i> , a ribbon fish, and <i>Regalecus russelii</i> , the oarfish rising to the surface	<i>Daphnia</i> spp. is highly susceptible to H <sub>2</sub> O <sub>2</sub> (Grant & Conlan, 2015; Reichwaldt et al., 2012)
(Gulakyan & Wilkinson, 2002)	1966 Earthquake, Lake Sevan	Lake Sevan, Armenia	<i>Cyclops strenuus</i> , <i>Acanthodiptomusdenticornis</i> , <i>Arctodiptomus ba-silifer</i> , <i>Arctodiptomus spinosus</i> , <i>Daphnia logispina</i> and <i>Keratella quadrata</i> Strong earthquakes result in the decrease of both biomass and the quantity of zooplankton	
(Witze, 2009; Grant et al., 2011)	M8.0 May 12, 2008 Sichuan Earthquake		Mass migrations of toads	
(Li et al., 2009)	M8 Wenchuan earthquake, 2008	Wenchuan	Disarray of circadian rhythms of laboratory mice before 2–3 days	
(Brancelj, 2021; Fidani, 2013; Galassi et al., 2014; Grant & Conlan, 2015)	M6.3 L'Aquila Earthquake6 April 2009	Italy(Gran Sasso Aquifer)	Mating <i>Bufo bufo</i> leaving their breeding pools 5 days before the earthquake Decline of <i>Nitocrellapescei</i> , <i>Diacyclospaoalae</i> , <i>Parastenocarislorenzae</i> and <i>Elaphoidellamabelae</i>	
(Kawagucci et al., 2012)	2011 Tohoku Earthquake	Japan	Increased whole microbial community number after 36 days with lower abundance of Archaeal 16S rRNA <i>Gammaproteobacteria</i> , <i>zeta-proteobacterial</i> phylogroup, <i>Desulfobacterales</i> phylogroup, <i>Desulfuromonadales</i> , <i>Arcobacter</i> ( <i>Epsilonproteobacteria</i> )	<i>Alphaproteobacteria</i> , phylum Proteobacteria, grows in abundance when interacting with ammonia-oxidizing archaea in the presence of H <sub>2</sub> O <sub>2</sub> because of its catalase activity (Bayer et al., 2019)
(Grant et al., 2015)	2011 M7 Contamana Earthquake	Yanachaga National Park, Peru	Ground dwelling birds ( <i>Galliformes</i> and <i>Tiniamiformes</i> ) terrestrial mammals (Carnivora, Cetartiodactyla, Cingulata, Perissodactyla, Primates and Rodentia) Rodents <i>Cingulata</i> (armadillos)	
(Natsuike et al., 2014)	2011 Great East Japan Earthquake in Funka Bay	Hokkaido, Japan	Changes in <i>Alexandriumtamarense</i> due to earthquake and induced tsunami	Hydrogen peroxide destructs the <i>Alexandrium</i> bloom (Burson et al., 2014)
(Kim et al., 2020)	M 5.8 Gyeongju earthquake, 2016	Korea	Dominant <i>Pseudomonas</i> and <i>Flavobacterium</i> , <i>Gammaproteobacteria</i> replaced by <i>Alphaproteobacteria</i> Disappearance of <i>Lysobacter</i> , <i>Nocardiopsis</i> , <i>Streptotrophomonas</i> , and <i>Streptomyces</i>	H <sub>2</sub> O <sub>2</sub> has a direct impact on <i>Pseudomonas</i> bacteria (Schmidt et al., 2006)

peroxide (Burson et al., 2014). However, the number of cysts increased significantly after the Tsunami. Another study highlights that the microbial community number increased after 36 days and decreased after 98 days during the 2011 Tohoku earthquake (Kawagucci et al., 2012). Studies suggest that the microbial communities may increase during the earthquake period, with *Gammaproteobacteria* being one of the affected organisms. Following the 5.6 magnitude Gyeongju Earthquake in South Korea, the primary microbial community was composed of *Pseudomonas* and *Flavobacterium* (Kim et al., 2020), although *Pseudomonas* is considered the least tolerant among bacterial groups based on past studies (Schmidt et al., 2006).

Studies have confirmed that changes in the geological and hydrological environment of groundwater before, during, and after an earthquake significantly affect benthic and obligate organisms living in the stratum. For example, the M6.3 L'Aquila earthquake in 2009 triggered the subterranean species of the Gran Sasso aquifer, resulting in the local extinction of some of the dominant copepods (Galassi et al., 2014). As a result of the earthquake, the groundwater ecology of the spring-fed by the Gran Sasso was also redistributed, leading to an increase in diversity

and evenness but a decline in their dominance (Fattorini et al., 2018). Similarly, in the Great Hanshin earthquake in January 1995, the sudden appearance of toxic *Microcystis aeruginosa* and the release of cyanotoxins were observed (Matsunaga et al., 1999). Several studies have reported that the introduction of peroxide can lead to a decrease in cyanobacterial biomass, which could result in the release of cyanotoxins (Lürling et al., 2014).

*Daphnia pulex* were found to be particularly impacted by hydrogen peroxide, and exhibited avoidance behavior when exposed to hydrogen peroxide. This evidence can explain the decrease of the *Daphnia* spp. prior to the earthquake (Grant & Conlan, 2015). Catalase activity plays a crucial role in the tolerance of organisms to hydrogen peroxide. Zooplankton having relatively less catalase activity than other bacteria can explain their higher susceptibility (Borgeraas & Hessen, 2002). Even if *Daphnia* spp. has catalase activity, high exposure to hydrogen peroxide can still have avoidance behaviour. Bayer et al. (2019) documented that *Alphaproteobacteria* thrive in the presence of hydrogen peroxide while interacting with ammonia-oxidizing archaea. It can be concluded that hydrogen peroxide has distinct effects on various species of bacteria.

This may explain the scenario of the Tohoku earthquake.

The impact of hydrogen peroxide on groundwater constituents can affect the nutrient sources available to microorganisms, while also hindering photosynthesis through the prevention of oxygen evolution and photosynthetic electron transport via hydroxyl radicals. This effect is comparable to the photo-inhibition observed in high Photosynthetically Active Radiation (PAR) or Ultraviolet B (UVB) radiation, which can cause significant damage to photosystem II resulting in oxidative stress, membrane damage, and pigment synthesis issues in green algae, diatoms, and other phytoplankton. While most phytoplankton cells can recover from photo-inhibition within hours, if these mechanisms are inadequate, permanent damage can occur. As cyanobacteria lack distinct organelles that store the photosynthetic apparatus,  $H_2O_2$  may have a more significant impact on cyanobacterial cells than on eukaryotic phytoplankton (Barrington & Ghadouani, 2008; Spooft et al., 2020). Changes in the microorganism's habitat can have potent effects on their catalase activities, and in some cases, can lead to death.

In summary, the following factors may be key drivers of changes in micro-organism communities:

**Disruption of Habitat:** Earthquakes have the potential to cause significant alterations to the physical environment, leading to the disturbance of habitats. Changes in pH, salinity, oxidative stress, and temperature resulting from seismic activity can affect the distribution and abundance of aquatic organisms, disrupt their life cycles, and impact breeding and feeding grounds. Furthermore, these changes can have cascading effects on the entire food chain, affecting organisms dependent on vegetation or microbiology.

**Species Interactions:** Earthquakes can disrupt established ecological relationships and modify species interactions. Shifts in habitat availability may increase competition for limited resources or introduce new predators and competitors. Such disruptions can have far-reaching consequences, influencing population dynamics and altering the composition of ecological communities.

**Displacement and Migration:** Earthquakes can trigger mass movements and displace organisms. Animals may relocate to seek suitable habitats and resources, leading to changes in population distributions and species composition in both affected and receiving areas.

It is important to recognize that the specific impacts of earthquakes on organisms can vary based on factors such as earthquake magnitude, proximity, ecosystem characteristics, and the resilience and adaptability of organisms. Additionally, the recovery and long-term effects on organisms and ecosystems following earthquake events are complex and may require an extended period of time for comprehensive assessment.

Although Table 4 does not offer a consistent set of criteria for direct seismic activity prediction, it suggests that a combination of indicators, when utilized alongside other monitoring tools, may hold potential for seismic activity forecasting.

#### 4. Possible link to earthquake early warning system

Several precursory phenomena, including geochemical, hydrogeological, ecological, and hydrochemical anomalies, have been reported to potentially indicate an impending earthquake. This review highlights 32 earthquake events where changes in groundwater chemistry were observed 5–6 months prior to the major quake, providing sufficient time for precautionary measures to be taken (Biagi et al., 2000; Chen & Wang, 2021; Kopylova & Boldina, 2021; Li et al., 2019). Establishing an effective network is essential for the success of early warning systems. This can be accomplished by strategically selecting monitoring sites near active fault lines and employing advanced sensors to track hydrogeochemical indicators such as hydrogen peroxide and hydroxyl radicals, and associated species with them. These sites would transmit data remotely, integrate with other seismic systems, and utilize machine learning for real-time analysis. This comprehensive, data-driven approach could significantly enhance earthquake early warning capabilities. Isotopic anomalies have been observed as precursors in

earthquakes with  $M > 5.0$ , such as in Iceland (Andr n et al., 2016; Barbieri et al., 2021; Skelton et al., 2014), Konya, India (Reddy et al., 2011), Xiajiang, China (Li et al., 2022; Shi et al., 2020), and Gyeongju, Korea (Kaown et al., 2019). These changes can be attributed to groundwater mixing, different groundwater sources, and rock-water interaction. Isotopic values of oxygen can increase because of the relation between  $\delta^2H$ ,  $\delta^{18}O$ , and  $H_2O_2$  (Barnette et al., 2011; Savarino & Thieme, 1999). The release of carbon dioxide is another major precursory phenomenon (Boschetti et al., 2019; Pierotti et al., 2015). All of these precursory geochemical and hydrochemical changes provide a possible model for earthquake prediction. Major changes in groundwater can have significant impacts on the behavior of organisms residing in those regions, as they depend on the physical and chemical properties of the water. Microorganisms are important bio-indicators of groundwater, and changes in temperature, pH, chemical composition, and turbidity can all affect aquatic life, potentially leading to death or changes in the microbiological community. The zooplanktonic community is particularly sensitive to peroxide (Escobar-Lux et al., 2020; Reichwaldt et al., 2012), and its biomarkers, such as phytadienes, mono- and diolefins (Alpar et al., 2012), can be used to identify it. Hydroxyl radicals can cause oxidative stress in microorganisms, resulting in damage to lipids, DNA, and proteins (Gutteridge, 1995). Thus, the biochemical changes can provide powerful insights as earthquake precursors. Considering this, the recordings of biochemical changes should also be prioritized because they can be a prominent earthquake precursory phenomenon.

However, changes in groundwater chemistry may not always be associated with seismic activity, as seasonal variations, rainfall, pollution, groundwater mixing, erosion, and temperature change can all affect it (Adekunle et al., 2007). Other factors like the introduction of fish and minnow, long-distance air pollution, snow melt, and breeding sites can also impact archaeal, zooplanktonic, and bacterial communities (Brancelj et al., 2012; Brancelj, 2021). Therefore, caution should be used in interpreting changes in groundwater chemistry and biology as seismic precursors. Nevertheless, anomalies in groundwater chemistry related to responses to hydrogen peroxide and hydroxyl radicals could potentially form a global early-warning earthquake forecast system.

#### 5. Conclusions and future research directions

Hydrogeochemical anomalies can occur prior to major earthquakes, particularly those with a magnitude greater than 5.0. These anomalies, which include changes in ionic, isotopic, organic, gaseous, and trace element composition, can be attributed to the increasing presence of hydrogen peroxide and hydroxyl radicals formed from reactions between holes and water at the rock-water interface. Along with ionic and organic changes, these anomalies can also affect microorganisms in groundwater, with zooplankton being highly susceptible to hydrogen peroxide and hydroxyl radicals leading to death and oxidative and DNA damage causing cellular function collapse. Thus, monitoring changes in groundwater biology may help predict seismic changes.

While previous investigations have focused on changes in ions, organics, and organisms in groundwater prior to earthquakes, this review emphasizes the significance of hydrogen peroxide and hydroxyl radical impacts that may offer a new avenue for forecasting major earthquake events. Nevertheless, it remains essential to develop robust tools and techniques for accurately identifying the origins of these species and the changes associated with them. Future research will require in-depth studies to achieve the proposed avenue of forecasting major earthquake events. Our literature review-based results indicate that redox reactions involving hydrogen peroxide, hydroxyl radicals, organic molecules, and ions could be responsible for many chemical changes observed in groundwater, however, the concentration of both species ( $\bullet OH$  and  $H_2O_2$ ) can change rapidly. Future research could focus on specific geological settings to investigate changes if specific ions, inorganic and/or organic species could provide a key to identify those chemical precursors or products that reflect highly stressed geological

formations. Geochemical and biological changes in groundwater may offer additional insights to establish a multi-parameters-based earthquake early-warning system. The effectiveness of such a system can be enhanced by deploying multi-parametric sensors capable of continuous real-time data collection and ensuring a centralized system for data integration and analysis. The unified monitoring network would facilitate the correlation of various anomalies with seismic activity, substantially improving earthquake early warning capabilities.

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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