



**HAL**  
open science

## A Review on the Elemental and Isotopic Geochemistry of Gallium

Wei Yuan, Jiubin Chen, Henry Teng, Benjamin Chetelat, Hongming Cai,  
Jincun Liu, Zaicong Wang, Julien Bouchez, Frederic Moynier, Jérôme  
Gaillardet, et al.

► **To cite this version:**

Wei Yuan, Jiubin Chen, Henry Teng, Benjamin Chetelat, Hongming Cai, et al.. A Review on the Elemental and Isotopic Geochemistry of Gallium. *Global Biogeochemical Cycles*, 2021, 35 (9), 10.1029/2021GB007033 . hal-03442865

**HAL Id: hal-03442865**

**<https://hal.science/hal-03442865v1>**

Submitted on 8 Aug 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Copyright

# Global Biogeochemical Cycles<sup>®</sup>

## REVIEW ARTICLE

10.1029/2021GB007033

### Key Points

- An overview of the geochemical properties of Ga in different reservoirs and a timely review of Ga isotope geochemistry
- A first tentative estimation of total masses of Ga in different compartments and trans-reservoir Ga flux based on the published data
- Broad applications of Ga and its isotopes in geosciences and related fields

### Supporting Information:

Supporting Information may be found in the online version of this article.

### Correspondence to:









J. Chen,  
[jbchen@tju.edu.cn](mailto:jbchen@tju.edu.cn)

### Citation:

Yuan, W., Chen, J., Teng, H., Chetelat, B., Cai, H., Liu, J., et al. (2021). A review on the elemental and isotopic geochemistry of gallium. *Global Biogeochemical Cycles*, 35, e2021GB007033. <https://doi.org/10.1029/2021GB007033>

Received 14 APR 2021  
Accepted 3 SEP 2021

## A Review on the Elemental and Isotopic Geochemistry of Gallium

Wei Yuan<sup>1</sup> , JiuBin Chen<sup>1</sup> , Henry Teng<sup>1</sup>, Benjamin Chetelat<sup>1</sup> , Hongming Cai<sup>1</sup>, Jincun Liu<sup>1</sup>, Zaicong Wang<sup>2</sup> , Julien Bouchez<sup>3</sup> , Frederic Moynier<sup>3</sup> , Jérôme Gaillardet<sup>3</sup> , Jacques Schott<sup>4</sup>, and Congqiang Liu<sup>1</sup> 

<sup>1</sup>School of Earth System Science, Institute of Surface-Earth System Science, Tianjin University, Tianjin, China, <sup>2</sup>School of Earth Sciences, State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences, Wuhan, China, <sup>3</sup>Université de Paris, Institute de Physique du Globe de Paris, CNRS UMR7154, Paris, France, <sup>4</sup>Géoscience Environnement Toulouse, CNRS (UMP 5563)-OMP-Université Paul-Sabatier, Toulouse, France

**Abstract** Gallium exhibits weak metallic properties owing to its proximity to non-metals in the periodic table, yet is volatile in extra-terrestrial bodies and fairly reactive in nature. It has been used extensively to elucidate the Solar System evolution, planet interior differentiation, and terrestrial processes. However, Ga speciation and transformation in various planetary compartments and the dynamics of its trans-reservoir pathways remain to be fully resolved. Although recent studies and the development of modern analytical techniques for Ga isotopes have markedly improved our understanding of Ga geochemistry, a systematical summary of state-of-the-art knowledge appears to be long overdue. Here we provide an overview of the geochemical properties of Ga in different reservoirs, including meteorites and Earth's interior and exterior compartments, and a timely review of Ga isotopic geochemistry. We also provide a first tentative estimate of total masses of Ga in different compartments and the trans-reservoir Ga flux, based on the published data. This compilation reveals clearly the lack of geochemistry data of Ga in Earth's interior, the imbalance of oceanic Ga budget and the potential implications of Ga isotopes, stimulating future systematic studies of Ga and its isotopes in geosciences and related fields.

### 1. Introduction

Gallium is a metallic member of the boron family (group IIIA; period 4; atomic number/weight 31/69.723) in the periodic table. The geochemistry of Ga has been a topic of considerable research over the past five decades, focusing chiefly on Ga concentration and speciation in various phases and environments (Benézéth et al., 1997; Burton et al., 1959; Fleischer, 1955; Persson et al., 2006; Rudnick & Fountain, 1995; Rudnick & Gao, 2003; Shaw, 1957; Shiller, 1988). It has been shown that Ga can be used to (a) distinguish terrigenous from marine environments in paleoclimate research (Chen et al., 1997), (b) trace sources of materials and constrain physiochemical conditions and dynamics of core-mantle differentiation (Blanchard et al., 2015; El Korh et al., 2017; Kato et al., 2017; McDonough & Sun, 1995), (c) identify genetic links between iron meteorites (Brown & Goldberg, 1949; Goldberg & Arrhenius, 1958; Kato et al., 2017; Lovering et al., 1957; Wai & Wasson, 1977), (d) explore the origin of volatile elements in the early Solar System, terrestrial planets, and the Moon (Kato & Moynier, 2017a, 2017b), and (e) make medical devices and therapeutic drugs (Blakemore et al., 1962; French et al., 1938; Goss et al., 2018; Matkovic & Gerber, 1992). A significant attribute of Ga is its proximity to the neighboring period-3 boron-group element Al. Gallium is a trace element with virtually no ability to form minerals of its own. However, the similarity of Ga and Al ensures the essential substitution of Al by Ga such that the trace element is often used as a geochemical analog of this major chemical constituent of silicate minerals (Burton et al., 1959; Diakonov et al., 1997; Orians & Bruland, 1988a, 1988b; Pokrovsky et al., 2004; Shiller, 1988). For example, taking advantage of the close relationship between Ga and Al, Ga has been used to investigate magmatic processes, metamorphic intensity, and surface sedimentation (Borisov & Saukov, 1960; Nesterenko et al., 1958). There are also non-trivial differences between Ga and Al in terms of their geochemical behavior in Earth's surface environment. As a result, such variances have been proved to be indicative of aqueous reaction pathways in marine and riverine environments, as well as of water-rock interactions in the context of weathering (Hieronymus et al., 1990; Orians & Bruland, 1988b; Shiller, 1988; Shiller & Frilot, 1996; Yamamoto et al., 1976).

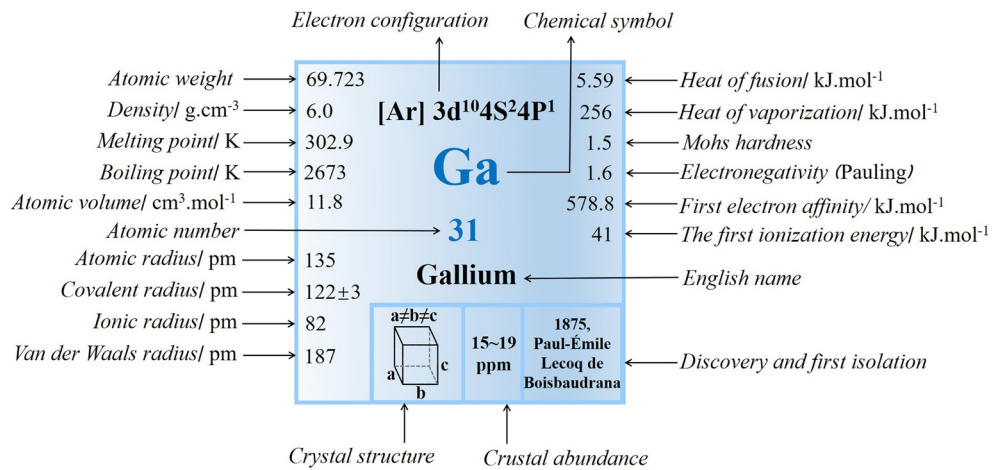
Unlike the mono-isotopic element Al, Ga has two stable isotopes,  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  (Laeter, 1972), which in principle can be more informative regarding tracing the geochemical and biogeochemical processes involving Al. However, due to the lack of effective means for separating Ga from complex matrices and limitations of conventional mass spectrometry, the isotopic geochemistry of Ga has been explored only in the very past. Although the recent development of multi-collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) and improvements in analyte purification methods have allowed accurate and precise measurements of isotopic ratios of many metals (e.g., Anbar et al., 2000; Maréchal et al., 1999; Zhu et al., 2000), methods for the accurate determination of Ga isotopic composition were not developed until 2016 (Kato et al., 2017; Yuan et al., 2016; Zhang et al., 2016). Processes and mechanisms triggering Ga isotopic fractionation are therefore yet to be fully elucidated. Nevertheless, preliminary studies (Kato et al., 2017; Yuan et al., 2016; Zhang et al., 2016) have provided data that clearly indicate the potential of Ga isotopes to trace its biogeochemical processes on Earth and beyond.

Here we provide a comprehensive review of Ga geochemistry and isotopic geochemistry. The motivation and rationale for this work was derived largely from the status quo that the previous review accomplished more than 60 years ago (Shaw, 1957). This review comprehensively discussed the history, chemistry, cosmic abundance, and geochemistry of Ga based on the limited literature published prior to 1956. In the light of advances in Ga chemistry over the past six decades, particularly recent breakthroughs in Ga isotopic geochemistry, it is clear that such a discourse is long overdue, looking back and summarizing progress to date and providing an updated view of Ga behavior in nature and the role it may play in advancing geochemistry and geoscience as a whole.

This review comprises three sections. First, a description of the physicochemical characteristics of Ga followed by a summary of its geochemical properties in different geological reservoirs such as meteorites, Earth's interior, and Earth surface systems (soils, sediments, hydrosphere, and biosphere), with a focus on Ga speciation in the aqueous environment. Then a tentative estimate of the total mass of Ga in different reservoirs and of Ga fluxes between them is presented. Finally, we provide an overview of recent progress in Ga isotopic geochemistry, ending with a discussion of the applications of Ga and its isotopes in geosciences and related fields.

## 2. Physicochemical Properties of Ga

Gallium was discovered by the French chemist Paul-Émile Lecoq de Boisbaudran in 1875 through the observation of its principal spectral lines in material separated from sphalerite (Shaw, 1957). Its electronic structure of  $[\text{Ar}]3d^{10}4s^24p^1$  (Figure 1) indicates that Ga is a metal element with possible valent states of +1 and +3. Although relatively equally distributed among the different Earth reservoirs, elemental Ga is rarely found in nature, with  $\text{Ga}^{3+}$  being the main form present in sphalerite and bauxite minerals (Hose, 2016; Shaw, 1957). Industrial elemental Ga is silver-white, always with a bluish tinge at ambient temperature and pressure due to surface oxidation. Ga crystals usually have an orthorhombic structure (space-group  $Cmca$ ), but the relatively low melting (302.9 K) and high boiling (2673 K) temperature ensure that pure elemental Ga can even melt in the human hand with little volatility owing to its low vapor pressure. Liquid Ga has a high tendency to cling to most materials (including glass) other than Teflon, graphite, and quartz, with care required when choosing a storage container for this metal. Gallium is of significant economic value as it is widely used in high-tech sectors such as electronics, the missile industry, and power supplies, and is commonly found in infrared circuits, light-emitting diodes (LEDs), and diode lasers (Katrak & Agarwal, 1981). To date, the biological behavior of Ga has remained unclear, although current understanding indicates potential medical applications. For example, it has been shown that Ga can disrupt bacterial Fe metabolism through a “Trojan horse” effect due to Fe-for-Ga surrogation resulting from the similar ionic radii of  $\text{Ga}^{3+}$  (0.62 Å) and  $\text{Fe}^{3+}$  (0.64 Å) (Burton et al., 1959). A potentially promising new therapeutic system for *Pseudomonas aeruginosa* infections taking advantage of the antimicrobial and antibiofilm ability of Ga has been approved by the US Food and Drug Administration, with large doses of Ga already being given to patients to treat hypercalcemia of malignancy (Merryman et al., 1994).



**Figure 1.** The physicochemical characteristics of Ga.

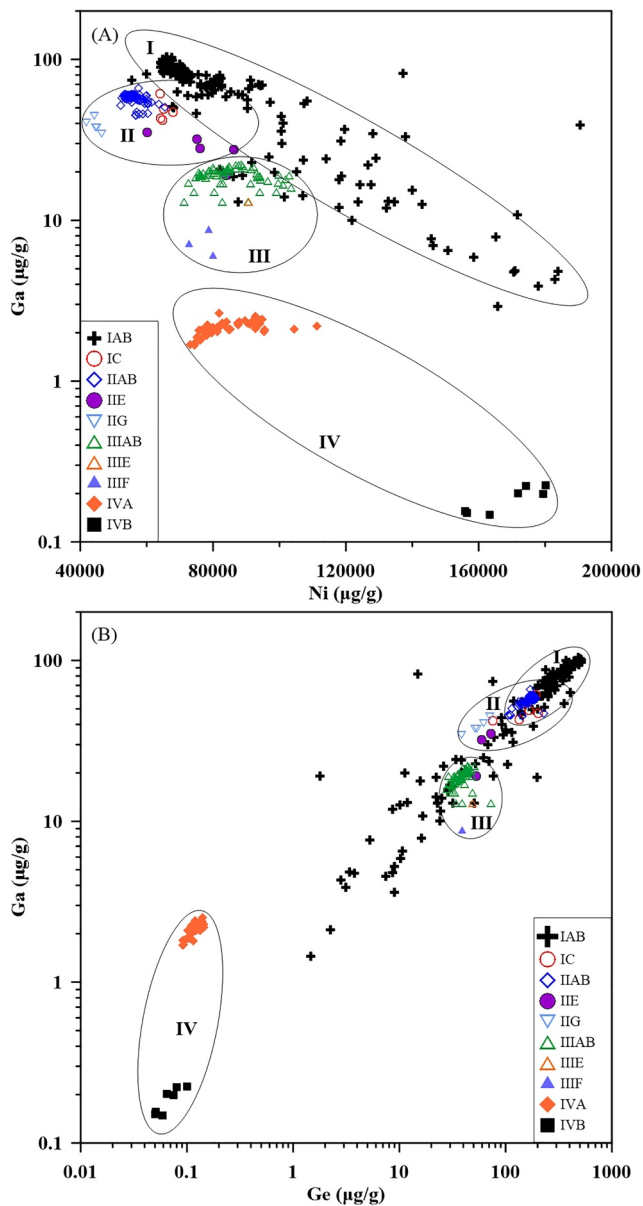
### 3. The Elemental Geochemistry of Ga

#### 3.1. Gallium in Meteorites

The first estimate of the solar abundance of Ga was approximately 2.36 (normalized to  $10^{12}$  atoms of H), obtained by Goldberg et al. (1960). However, the emission line of Ga was quite perturbed and the estimate was based on complex solar atmospheric models, so this value should be considered as having significant uncertainty (Bidelman & Corliss, 1962; Goldberg et al., 1960; King et al., 1965). A recent investigation gave an estimate of  $2.88 \pm 0.10$  for solar Ga abundance (Grevesse & Sauval, 2002; Lodders, 2003; Lodders et al., 2009).

Cosmochemically, Ga is considered a moderately siderophilic element with preferential partition into metal phases relative to silicates (Lovering et al., 1957; Wai & Wasson, 1977, 1979; Wasson, 1967b). As a consequence, it is generally enriched in iron meteorites (at up to 100 ppm; Lovering et al., 1957), representing the metallic cores of planetary bodies relative to undifferentiated chondritic meteorites (5–10 ppm; Lodders, 2003). Relatively high Ga concentrations occur in the sulfide phase of chondrites, indicating that it may also be chalcophilic under reducing conditions (Allen & Mason, 1973; Lovering et al., 1957). Gallium is more volatile than the rock-forming elements Fe, Mg, and Si (Albarède, 2009). Definition of the volatility of individual elements under solar nebular conditions as the 50% condensation temperature ( $T_{50\%}$ , K) would mean that Ga has a  $T_{50\%}$  of 968 K, 25–30% lower than that of Fe, Mg, and Si ( $T_{50\%} = 1300\text{--}1400$  K, Albarède, 2009; Lodders, 2003), suggesting potential applications of Ga in tracing volatile evolution of the Solar System. For example, carbonaceous chondrites exhibit progressive depletion in Ga across the CI, CM, and CV groups, correlated with a general depletion in volatile elements (Kato et al., 2017; Lodders & Fegley, 1998; Lodders et al., 2009; McDonough & Sun, 1995). The moderate volatility of Ga implies it is depleted in planetary bodies that have experienced strong volatile depletion, such as the Moon (Kato & Moynier, 2017b).

The siderophilic nature of Ga (Mann et al., 2009; Siebert et al., 2011) means it is generally enriched in planetary cores (therefore becomes one of the most abundant elements in the cores), so Ga content can also aid the tracing of evolutionary histories of iron meteorites parent bodies. Depending on the extent of volatile depletion in parent bodies and core-mantle differentiation conditions, Ga concentrations span a range of up to two orders of magnitude across various iron meteorites (Akaiwa, 1966; Allen & Mason, 1973; Baedecker & Wasson, 1970; Cobb, 1967; Cobb & Moran, 1965; Davis, 2006; Fouché & Smales, 1967; Greenland, 1965; Hecht & Fenninger, 1965; Onishi & Sandell, 1956; Schaudy et al., 1967; Tandon & Wasson, 1968; Wasson, 1967a, 1967b). Goldberg et al. (1951) initially classified iron meteorites into three groups based mainly on Ga content. Both Ga and Ge are moderately volatile elements that are not substantially fractionated during fractional crystallization (Davis, 2006; Lovering et al., 1957), so the concentration ratio of Ga or Ge to the refractory element Ni is a key measure reflecting volatile depletion in iron meteorite



**Figure 2.** Ga versus Ni (a) and Ge (b) concentrations in the classification of iron meteorites. Four main groups and several subclass (IAB ~ IVB) of iron meteorites were obtained based on the Ga, Ni, and Ge concentration and the structure of meteorites (Campbell & Humayun, 2005; Choi et al., 1995; Cobb & Moran, 1965; Lovering et al., 1957; Wasson, 1999; Wasson & Choe, 2009; Wasson & Kallemeyn, 2002; Wasson & Richardson, 2001; Wasson et al., 2007).

parent bodies. These ratios have been used in the classification of iron meteorites to distinguish different parent bodies (asteroids) from which individual meteorites originate (Figure 2 and Table S1; Davis, 2006; Kato et al., 2017; Lovering et al., 1957; Wai & Wasson, 1977, 1979). Four groups are generally classified (Figure 2): groups I, II, III, and IV, with Ga contents range of 80–100, 40–65, 8–24, and 1–3 ppm, respectively (Cobb & Moran, 1965; Lovering et al., 1957). The subclasses IAB-IVB of iron meteorites are also obtained based on Ga, Ni, and Ge contents and meteorite structure (Campbell & Humayun, 2005; Choi et al., 1995; Cobb & Moran, 1965; Davis, 2006; Lovering et al., 1957; Wasson, 1999; Wasson & Choe, 2009; Wasson & Kallemeyn, 2002; Wasson & Richardson, 2001; Wasson et al., 2007).

Gallium has been used to constrain the first solid origin of the Solar System, the Ca-Al-rich inclusions (CAIs; Connelly et al., 2012; Grossman et al., 2002; Kato & Moynier, 2017a). Although formed at high-temperature and generally depleted in volatile elements, CAIs are surprisingly enriched in Ga with an average content of up to 18 ppm, about twice that of CI chondrites (9.5 ppm; Kato & Moynier, 2017a). Secondary alteration of CAIs in the parent body and gas-solid exchange in solar nebulae prior to parent body formation are two possibilities for explaining this enrichment (and also that of moderately volatile Zn; Kato & Moynier, 2017a), but the cause is still debated (Bischoff et al., 1987; Chen-Lin et al., 1976; Sylvester et al., 1993).

### 3.2. Gallium in Earth's Interior

Limited information is available concerning the systematics of Ga in Earth's interior. However, as it lacks a strong affinity for either siderophile or lithophile elements, Ga may not be particularly enriched or depleted in Earth's interior or lithosphere (Kato et al., 2017; McDonough, 2003; McDonough & Sun, 1995). A recent study estimated an average concentration of  $2.4 \pm 1.9$  to  $5.3 \pm 2.3$  ppm in Earth's core (Blanchard et al., 2015), depending on how the calculation was performed. This is significantly below the estimated mean content of  $\sim 8.7$  ppm for the lithosphere (Li, 1985), but is consistent with the estimated Ga content of Earth's mantle ( $\sim 4$  ppm) based on the chemical systematics of Al, Sc and Ga in basalts and peridotites (McDonough & Sun, 1995; McDonough, 1990a, 1990b, 2003; O'Neill & Palme, 1998; Sun, 1982). This suggests that Ga may not have behaved as a typical siderophile element during Earth's accretion. The possible cause is that the conditions of Earth's core formation at high temperature and pressure reduce the siderophilic behavior of Ga compared with prevailing conditions (temperature and pressure) for the formation of iron meteorite parent bodies (Blanchard et al., 2015; Kato & Moynier, 2017a).

Gallium contents of various minerals and rocks are summarized in Table S2. In general, Ga content is in the range of 0.1–26 ppm for mantle peridotites and 0.2–81.1 ppm for basaltic magmas (Polat et al., 2009; Savov et al., 2007; Shafer et al., 2004; Sun et al., 2017). It is a moderately incompatible trace element during magmatic processes with an enrichment factor in basaltic lavas similar to that of Al (McDonough, 1990a; Sun, 1982). It may also be used as an indicator of mantle material transfer (Davis et al., 2013; El Korh et al., 2017; Munir, 2018; O'Neill & Palme, 1998). The heterogeneity of Ga among different compartments is clearly evident in subduction zones, with subducted sediment having almost the same Ga contents (marine sediments, 22 ppm) as oce-



anic crust (mid-ocean-ridge basalt (MORB), 17.5 ppm), much higher than that of the lithospheric mantle (spinel peridotite xenoliths, 2.4 ppm; Burton et al., 1959; Gale et al., 2013; McDonough, 1990b).

Magmatic processes may impact Ga distribution and its mineral phase transformation. Prokof'Ev et al. (2016) reported a Ga content of 0.5–495 ppm (average 18 ppm) for magmatic melts based on 2688 analyses of natural magmatic melts. The average Ga content of magmatic rocks is broadly similar to its crustal abundance, but higher than that of most sedimentary rocks (barring shales; Burton et al., 1959; Sandell, 1949; Shaw, 1957). The mean Ga content of magmatic rocks is about twice that of siliceous sedimentary rocks (~10 ppm; Burton et al., 1959; Culkin & Riley, 1958a, 1958b). During fractional crystallization, the Ga content of MORB lava flows (12–25 ppm) varies by tens of percent, with a negative correlation with  $Mg^{\#}$  value (40–70;  $Mg^{\#} = 100 \times (Mg/(Mg + 0.85 \times Fe))$ ) (Yang et al., 2020). As for other first-row transition elements, the Ga mineral-melt partition coefficients may be used to predict the mineralogical compositions and degree of melting of the source (Davis et al., 2013; Le Roux et al., 2015). Gallium is usually incompatible in olivine and moderately incompatible to compatible in pyroxenes, leading to different mineral-melt partition coefficients,  $D_{Ga}^{mineral/melt}$ . Few Ga partition coefficients were determined experimentally in early studies, with values of 0.024, 0.19, 0.86, and 4.6 for forsterite, diopside, anorthite, and spinel, respectively, obtained for the forsterite-anorthite-diopside system at one atmosphere pressure and 1300°C (Malvin & Drake, 1987). Later, ranges of values were obtained by Macdonald et al. (2010) for other minerals, with partition coefficients of 1.1–1.4, 0.11–0.20, <0.01–0.37, 0.36–0.37, 2.2, 0.02, and 12 for alkali feldspar, hedenbergite, fayalite, amphibole, biotite, ilmenite, and chevkinite, respectively. Le Roux et al. (2015) determined respective  $D_{Ga}^{Opx/melt}$  and  $D_{Ga}^{Cpx/melt}$  values of 0.23 and 0.28 at low pressure (1.5 GPa) for ortho- and clino-pyroxene (Opx and Cpx) in spinel peridotite melting, with higher values of 0.42 and 0.40 at intermediate pressure (2.8 GPa); for garnet peridotite melting, the respective values were 0.38 and 0.37 at 3 GPa, decreasing to 0.26 and 0.30 with pressures of up to 4 GPa. A  $D_{Ga}^{Cpx/melt}$  value of 0.78 was suggested for partitioning in MORB-like eclogite melting at 2–3 GPa. Small variations in partition coefficient are clearly incompatible with the large Ga content variation in natural samples (Table S2), thus further systematic examination is needed to better constrain Ga partitioning between different mineral phases and to explore the potential implications for mineralization and magmatism.

Although natural Ga reserves are greater than those of Cu, Ag, and Zn, Ga rarely forms independent or high-content minerals. Söhngelite ( $Ga(OH)_3$ ) and gallite ( $CuGaS_2$ ) are the only two natural crystalline phases known to host Ga stoichiometrically (Négrell et al., 2018; Strunz, 1965; Strunz et al., 1958); but, despite the rarity of such minerals, Ga commonly occurs in various rock types (e.g., sphalerite, magnetite, and silicates) as a trace element substituted for Zn, Fe, or Al (Burton et al., 1959). Across various minerals and rocks on the Earth, the Ga content of graphite is generally higher than that of other non-silicate minerals and silicate minerals such as pyroxenes, olivine, and quartz (Table S2; Borisenok & Saukov, 1960; Burton et al., 1959). Higher Ga content of up to 170 ppm has been reported for mica (Burton et al., 1959). Coals are commonly enriched in Ga, at up to 1,500 ppm and often at industrial grades (Qin et al., 2015), with its primary carriers being organic matters and clay minerals such as boehmite and diaspore.

The Ga distribution in metamorphic rocks has attracted little attention as few data have become available since the 1957 review (Shaw, 1957). Early studies indicate that the Ga content of metamorphosed igneous rocks (9–18 ppm, average 12 ppm) is usually lower than that of metamorphosed sedimentary rocks (2–37 ppm, average 19 ppm); with Al-rich/Si-poor and Si-rich/Al-poor minerals having higher and lower Ga contents, respectively (Ahrens, 1954; Burton et al., 1959; Daly, 1933; Fleischer, 1955; Rankama, 1946; Shaw, 1957). Regardless of the nature of the protolith, it seems that metamorphism may modify Ga distributions in parental rocks. Although the Ga content and Ga/Al ratio of most metamorphic rocks are similar to those of unmetamorphosed rocks (Borisenok & Saukov, 1960; Evans, 1964; Higazy, 1952; Nesterenko et al., 1958; Nockolds & Mitchell, 1948), particular Ga distribution patterns in certain metamorphic minerals have been observed. For example, significant Ga enrichment occurs in garnet during skarn formation (Nesterenko et al., 1958), in epidote during the last mineralization stage, and in vesuvianite skarn during the pneumatolytic stage (Borisenok & Saukov, 1960). Changes in metamorphic intensity or stage may also cause variations in Ga content and/or Ga/Al ratios (Evans, 1964; Higazy, 1952), as in greisenization and albitization during metamorphism of granitic rocks (Sitnin, 1960).

The distribution of Ga among different mineral phases may result from a number of factors including strong bonding of Ga with organic matter (e.g., graphite), isomorphism with Al and Fe, and adsorption on clay minerals and iron oxides. The chemical similarity of Ga and Al (Ahrens, 1964; Clarke & Martell, 1992; Diakonov, 1995; Pokrovski et al., 2003) is based largely on their same ground-state electronic configurations (Ahrens, 1964; Clarke & Martell, 1992). Gallium content and Ga/Al ratios can thus be used to characterize rocks and trace geological processes in the deep Earth. For example, the Ga/Al ratio is commonly used to identify the petrological group to which igneous rocks belong. De Argollo and Schilling (1978) reported a variation in Ga/Al ratios by up to 62% in volcanic rocks, with ratios increasing with  $\text{Al}_2\text{O}_3$  content (from 10.2 to 19.4 wt.%) but decreasing with  $\text{SiO}_2$  content (from 54.1 to 36.3 wt.%). The Ga/Al ratio in Al oxides ( $2.7 \times 10^{-4}$ ) is similar to that in marine clays ( $2.4 \times 10^{-4}$ ; Burton et al., 1959; Schulte & Foley, 2013). Owing to the similarity of  $\text{Ga}^{3+}$  and  $\text{Fe}^{3+}$  ionic radii (0.62 Å and 0.64 Å, respectively) and ionization potentials, Ga can also substitute for  $\text{Fe}^{3+}$ . This may explain the commonly observed relationships between  $\text{Ga}^{3+}$  and  $\text{Fe}^{3+}$  concentrations in rock and sediment samples, and the high Ga contents of Fe-bearing minerals such as magnetite (20–90 ppm; Burton et al., 1959). Similar isomorphous substitution occurs with Cr (ionic radius of 0.63 Å; Burton et al., 1959), although  $\text{Ga}^{3+}$  substitution for  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$  has not been investigated thoroughly, as the few studies reported involved artificially Ga-doped materials such as sulfides, silicates, and germanates considered as analogs of Al minerals (Goodyear & Steigmann, 1963; Pentinghaus & Bambauer, 1971). Improved understanding of the genesis of Ga-bearing minerals or ore deposits therefore requires further systematic study to better constrain the incorporation of Ga in different crystalline phases.

Gallium's incompatibility and solubility in fluids are also key factors controlling its geochemical behavior and partitioning between mineral phases, and can be used to track hydrothermal processes (Davis et al., 2013; El Korh et al., 2017; Munir, 2018). The dual lithophile-chalcophile characteristics of Ga are discriminable in its distribution in hydrothermalism. For example, sphalerite Ga contents are relatively high and usually correlated with Zn content, as Ga reacts as an isomorphous substitute for Zn in sulfides (Burton et al., 1959; Fryklund & Fletcher, 1956; Vershkovskaya & Fabrikova, 1957), whereas quartz-fluorite veins formed under low-temperature hydrothermal conditions have relatively low Ga contents (Frenzel et al., 2016; Vershkovskaya & Fabrikova, 1957). Interaction with country rocks may also impact the distribution of Ga among minerals, with such interaction reducing the reactivity of Ga, resulting in high Ga contents in sphalerites formed at low temperature (Vershkovskaya & Fabrikova, 1957). Later processes such as oxidation and alteration in subsurface regions may also change the concentration and speciation of Ga in minerals at depth with, for example, Ga contents being low in co-existing Zn- and Pb-rich minerals, especially plumbojarosite and hydrogothite. The precipitation of Ga with hydroxides is another important factor controlling its redistribution in the oxidized zone where Al and Fe oxihydroxides usually form (Razekov & Galaktionova, 1962).

Although the above studies have significantly improved our knowledge of Ga geochemistry in the Earth interior, processes and related mechanisms controlling Ga distribution among minerals and reservoirs remain unclear. New systematic studies are needed to build a more comprehensive understanding of Ga geochemistry in the Earth interior.

### 3.3. Gallium in Soils and Sediments

Gallium and Al are not particularly mobile during weathering (Poedniok, 2008), as indicated by bauxite deposits (formed primarily by intense weathering of aluminosilicate rocks) having higher contents of both elements relative to, for example, limestone; with a mean Ga/Al ratio of  $2.7 \times 10^{-4}$ , similar to the crustal value (Bennett & Czechowski, 1980; Poedniok, 2008; Schulte & Foley, 2013). However, the chemical dissimilarity of Ga and Al during weathering is indicated by changes in Ga/Al ratios in soil profiles, with Ga content increasing with weathering intensity (clay content), although currently available data indicate no trends in Ga/Al ratios with depth in soil profiles (Turton & Mulcahy, 1962). For example, the average Ga/Al ratio in saprolite ( $2.1 \times 10^{-4}$ ) is lower than that of the regolith for basaltic weathering ( $2.6 \times 10^{-4}$ ) (Hieronymus et al., 2001). The divergence of Al and Ga during weathering may be due to their solubility difference, with Ga being slightly more leachable from minerals than Al or Fe, resulting in fractionation of Ga/Al and Fe/Al ratios during certain weathering, erosion, and transportation processes (Sections 3.4.1 and 3.4.2), where

Ga is preferentially released to solution (Alina, 2010; Welch et al., 2004). Furthermore, Ga hydroxides have lower solubility than Al or Fe hydroxides and tend to be enriched in authigenic sedimentary phases. Finally, within the framework of hard/soft acid/base (HSAB) theory (Pearson, 1963), Ga hydroxide is a stronger acid (weaker base) than Al hydroxide, implying a difference in pH-dependent behavior in processes such as oxidative dissolution of sulfide ores (Razenkova & Galaktionova, 1962).

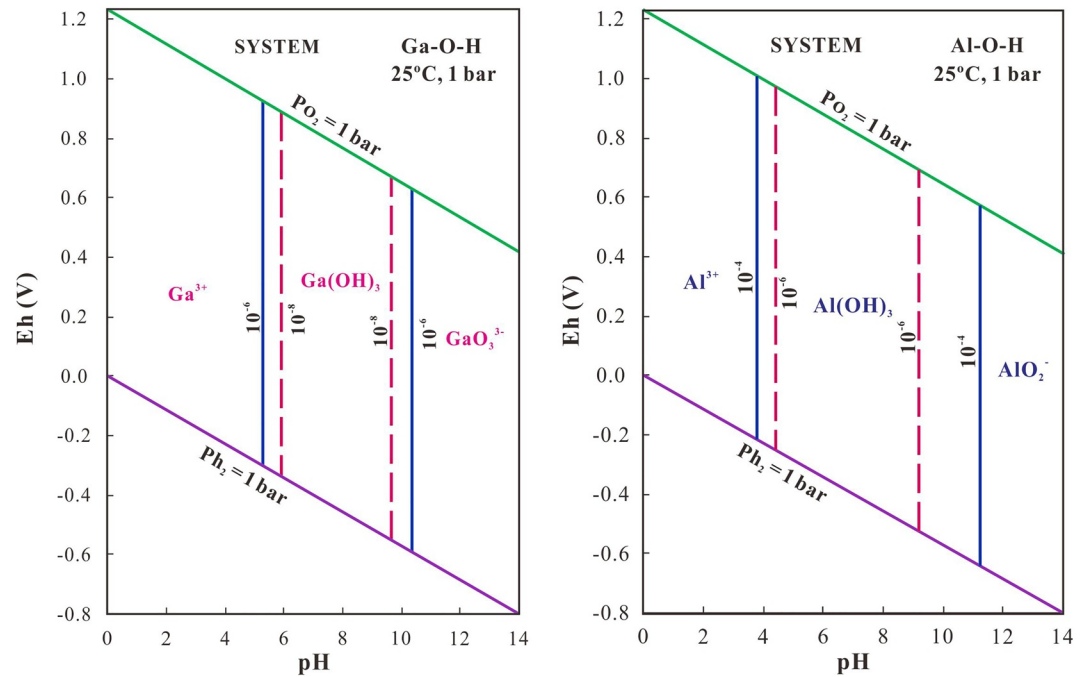
Soils are derived predominantly from continental weathering, and their Ga contents are strongly influenced by the compositions of their parental rocks and minerals. Bowen (1982) estimated an average Ga content of 21 ppm for 1,600 soil samples collected globally, with a range of 1–70 ppm, partially exceeding the crustal content of 15–19 ppm (Munir, 2018). Recent studies have shown soil Ga contents mainly within this range (Nuamah et al., 2019; Wang et al., 2020), which is not unexpected given the strong affinity of Ga with clay minerals, organic matter, and Fe-Mn hydroxides. Gallium is commonly enriched in residues of intense weathering, but with lower the Ga/Al ratios (Butler, 1953, 1954). This trend is controlled not only by the breakdown rate of Ga-containing minerals, but also by the rate of formation of secondary phases into which Ga is incorporated. Some studies have found that the Ga content of sedimentary rocks (e.g., bauxite) and sediments (e.g., lake muds) formed under reducing conditions are higher than those in similar materials formed under oxidizing conditions, suggesting a possible redox impact on the Ga distribution (Gorham & Swaine, 1965; Wolfenden, 1965).

Knowledge of Ga speciation in soils is of utmost importance in characterizing its physiological toxicity, bioavailability, migration, and transformation at Earth's surface, but very limited information is available. Połedniok (2008) investigated the speciation of Ga in brown (high nutrient content) and white (low nutrient content) soil from respective industrial and agricultural regions of Poland, using a sequential extraction method modified from Tessier et al. (1979) to separate soil Ga into exchangeable, carbonate, Fe-Mn oxide, organic, and residual fractions. Results indicate that the Ga content of industrial soils is generally higher than that of agricultural soils, with the proportion of bulk Ga in each fraction varying considerably in the order of organic > Fe-Mn oxide > exchangeable > residual for industrial soil and exchangeable > organic > Fe-Mn oxide for agricultural soil. This difference was attributed to soil type and human activity including industrial emissions and fertilizer application (Połedniok, 2008).

Just as soils are the main sink of residues from water-rock interactions, aquatic sediments are complement recipients of surface weathering products. Previous studies of Ga geochemistry in sediments started with the measurement of the Ga content in marine particles. A pioneering study by Goldschmidt and Peters (1933) reported commonly higher Ga contents for red clays (4–22 ppm) than silica (4–7 ppm) and calcium mud (~4 ppm). Goldberg and Arrhenius (1958) determined the Ga content of marine sediments in the eastern Pacific Ocean, reporting values of 19–22 ppm (mean 21 ppm) in black-brown clay. Burton et al. (1959) found a similar Ga content for other marine clay samples (20–28 ppm, mean 22.4 ppm). The Ga content of siliceous and calcareous oozes generally displays a significant negative correlation with silica and carbonate mineral contents, with a higher content (up to 20 ppm) in extracted clay phases (Burton et al., 1959). The average Ga/Al ratio of these marine clays ( $2.40 \times 10^{-4}$ ) is similar to that of granitic rocks ( $2.35 \times 10^{-4}$ ), indicating no significant differentiation of Ga and Al during the weathering of terrestrial rocks, transport of detrital sediments, or deposition of sediments as clays on the ocean floor (Burton et al., 1959). Together, these observations indicate that in most authigenic marine sediments, Ga is hosted mainly by detrital fractions. However, the oxide phases of marine sediments, for example, manganese nodules, have significantly higher Ga/Al ratios ( $9.7 \times 10^{-4}$ ) than marine clays ( $2.40 \times 10^{-4}$ ), despite their similar ranges in Ga content (15.7–21.5 ppm). This ratio is lower than that of seawater ( $3 \times 10^{-3}$ ), implying Ga-Al fractionation during incorporation into manganese nodules (Goldberg & Arrhenius, 1958).

To summarize, Ga, together with Al and/or Fe, may be a useful tool in elucidating the behaviors of trivalent elements (e.g., Sc and Ti) during weathering. More importantly, the strong association of Ga with widely distributed Fe solid phases must be considered when interpreting the distribution of Ga in various surface environments. Whether Ga forms organometallic complexes in soils, and the quantitative impact of such compounds on the Ga distribution in soils, remain to be clarified (Połedniok, 2008). The potential application of Ga in tracing and characterizing relative geochemical reactions in soils and weathering processes has yet to be fully explored.





**Figure 3.** Eh-pH diagram of Ga (a) and Al (b). The assumed activities for the dissolved species are  $10^{-8}$  for Ga, and for  $10^{-4}$ ,  $10^{-6}$  Al (Brookins, 1988).

### 3.4. Gallium in the Hydrosphere

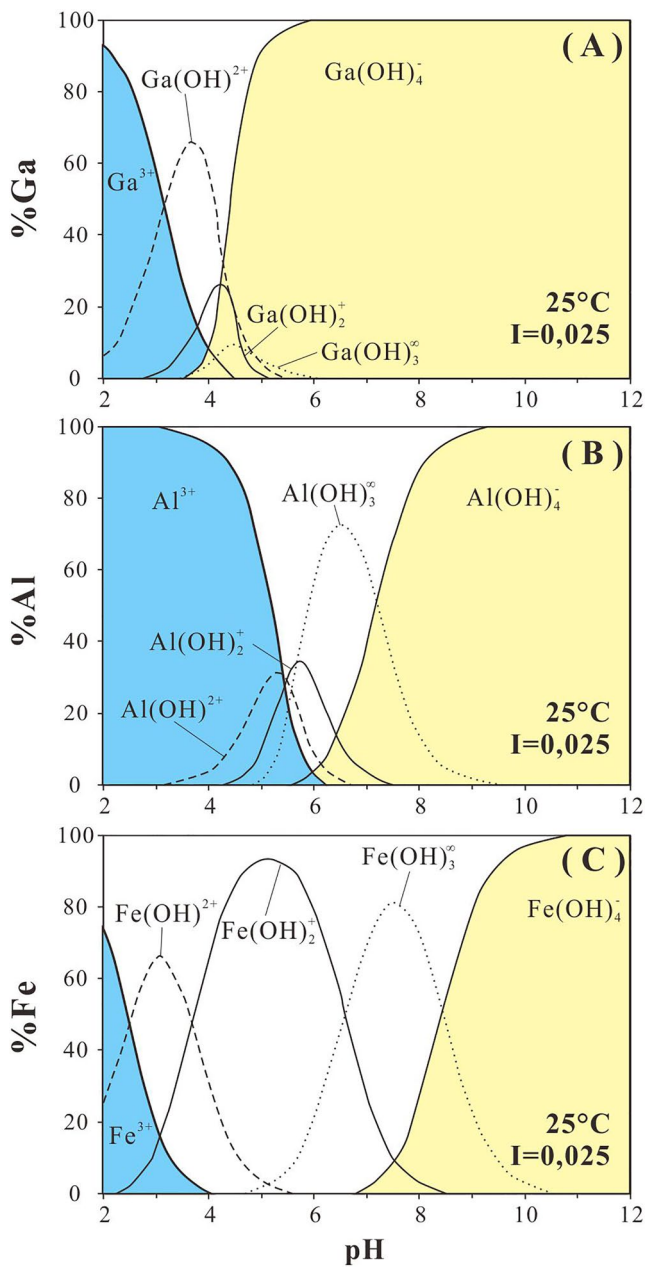
In addition to release from minerals by chemical weathering, dissolution, adsorption, and (co-)precipitation associated with biogeochemical processes may control the abundance and speciation of Ga in aqueous environments (Balistrieri et al., 2003; Paulson & Balistrieri, 1999; Pokrovsky et al., 2004). The aqueous geochemistry of Ga and the relative roles of the various processes in aquatic systems are discussed in the following sections.

#### 3.4.1. Characteristics and Transformation of Ga Species in Aqueous Solution

Gallium and Al display similar speciation in aqueous solution in the Eh-pH diagram (Figure 3), implying that Ga acts as an analog of Al in aquatic systems. Under acidic and alkaline conditions, Ga and Al exist as trivalent cations ( $\text{Ga}^{3+}$ ,  $\text{Al}^{3+}$ ) and corresponding oxyanions ( $\text{GaO}_3^{3-}$  and  $\text{AlO}_3^{3-}$ ). In intermediate pH ranges (5.3–10.4 for Ga and 3.7–11.3 for Al), the metal hydroxides  $\text{Ga}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  are the predominant species (Brookins, 1988). Thermodynamic data for Ga and Al are summarized in Table S3.

Few studies have investigated the speciation of Ga in aqueous solutions under different physicochemical conditions (Benézéth et al., 1997; Diakonov et al., 1997; Persson et al., 2006; Pokrovsky et al., 2004). The Bjerrum plot (Figure 4a) describes the distribution of monomeric Ga species as a function of pH at 25°C, with Ga aqueous concentrations of  $\leq 10^{-9}$  M, indicating the following. The hydrolysis of  $\text{Ga}^{3+}$  occurs at pH values as low as 2, with successive formation of  $\text{GaOH}^{2+}$ ,  $\text{Ga}(\text{OH})_2^+$ ,  $\text{Ga}(\text{OH})_3$ , and  $\text{Ga}(\text{OH})_4^-$  as pH increases and with  $\text{Ga}(\text{OH})_4^-$  being the dominant species in the pH range of natural waters. At constant pH, the degree of  $\text{Ga}^{3+}$  hydrolysis increases with temperature. As the aqueous Ga concentration increases, polynuclear species form, leading to precipitation of amorphous  $\text{Ga}(\text{OH})_3$  (Figure 4).

A comparison of Ga aqueous species distribution (Figure 4a) with those of Al and Fe (Figures 4b and 4c) indicates that, consistent with HSAB classification of (Pearson, 1963), hydrolysis of the harder  $\text{Al}^{3+}$  aqueous ion (through complexation with  $\text{OH}^-$ ) would not occur as readily as that of the softer  $\text{Ga}^{3+}$  and  $\text{Fe}^{3+}$ , with  $\text{Ga}(\text{OH})_4^-$  dominating Ga speciation in the pH range of most natural fluids (Benézéth et al., 1997; Diakonov, 1995; Persson et al., 2006). Mononuclear and small polynuclear species of Fe(III) are less stable



**Figure 4.** Distribution of monomeric Ga(a), Al (b), and Fe(III) (c) species as a function of pH at 25°C, excluding polymeric species ( $[Ga(aq)] \leq 10^{-9}$  M,  $[Al(aq)] \leq 10^{-8}$  M;  $[Fe(III)(aq)] \leq 10^{-10}$  M). After Diakonov (1995).

than their Ga and Al analogs, so large polymers with  $\beta$ -FeOOH-like structures (i.e.,  $Fe_{24}$  polycations) for rapidly during Fe(III) hydrolysis, leading to the precipitation of Fe oxy-hydroxides (Pokrovsky & Schott, 2002b). In contrast,  $Al^{3+}$  forms more stable complexes with  $F^-$  than  $Ga^{3+}$  and  $Fe^{3+}$ , and with ligand harder than  $OH^-$  or  $Cl^-$ . HSAB concepts thus provide useful information concerning the affinity of  $Ga^{3+}$  with various inorganic and organic ligands or solid surfaces in solutions, with respect to that of  $Al^{3+}$ .

An X-ray adsorption fine structure study of  $Ga^{3+}$  hydrolysis under various pH conditions (Pokrovsky & Schott, 2002a) has shown that  $Ga^{3+}$  hydrolyzes via the formation of Ga oxy-hydroxide polynuclear species composed of  $Ga(O/OH/H_2O)$  octahedron. The degree of edge/corner sharing amongst the octahedra appears to be pH-dependent (Figure 5). At  $pH \geq 4$ , the  $Ga_{13}$  Keggin type polycation, in which 12 edge-linked Ga octahedra surround a central tetrahedral Ga atom, dominates Ga speciation (Figure 5). At  $pH > 4.5$ , the  $Ga_{13}$  cation transforms into more disordered  $GaOOH-Ga(OH)_3$  precursors. The  $Ga_{13}$  polycation has the same local structure as the  $Al_{13}$  polycation formed during  $Al^{3+}$  hydrolysis. The sensitivity of Ga speciation to physicochemical conditions in aqueous solution implies that Ga may be applicable as a tracer of how such conditions changed in ancient aqueous environments.

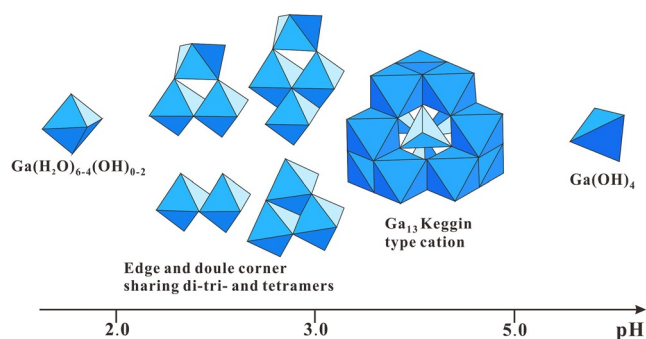
Adsorption is a non-trivial behavior of high-valence ( $>2$ ) elements in solution, and is particularly relevant to natural aqueous environments where suspended particles such as mineral grains and aggregates of organic matter commonly occur. Such particles can transport large amounts of these elements directly (especially insoluble trace elements such as those of the groups IIIA and IVA), or act as substrates for adsorption of trivalent and tetravalent elements such as Ga, Al, and many others (e.g., Sc, Ti, Cr, Ge, Y, Zr, In, Hf or Tl; Balistrieri et al., 2003; Dupré et al., 1999; Gaillardet et al., 2003; Paulson & Balistrieri, 1999; Pokrovski et al., 2002; Pokrovsky & Schott, 2002b).

Few studies have reported experimental results on the adsorption of Ga on mineral surfaces. Persson et al. (2006) and Pokrovsky et al. (2004) examined aqueous Ga species in the presence of calcite and goethite and found that pH and adsorbent concentrations greatly affect the amount of adsorbed Ga and Ga speciation, both in solution and on adsorbent surfaces (Figure 5). The observed pH dependence is expected from the surface charge properties of calcite and goethite (Figure 6). Gallium behavior during mineral coprecipitation has rarely been reported.

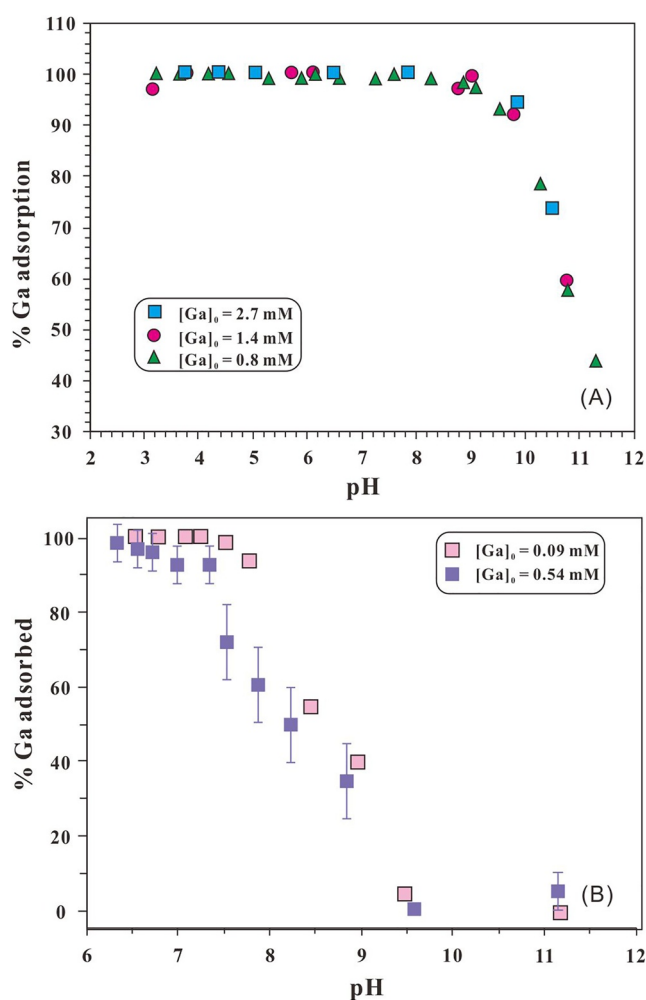
### 3.4.2. Gallium in Riverine Systems

Gallium is generally more mobile than Fe and Al in erosion and transport processes (Figure 7; Gaillardet et al., 2004), and small geochemical differences may induce fractionation of the three elements during surface weathering (Burton et al., 1959; Wood & Samson, 2006). For

example, compared with soils, Ga/Al ratios are significantly variable across aquatic environments (Tables 1 and S4–S8), even with variations within a single water column (Table 1). Furthermore, although Ga and Al may have the same sources and display similar geochemical behaviors during weathering, dissolved Ga/Al ratios are consistently higher than in related solid materials, by up to three orders of magnitude (Brown et al., 2010; Kramer et al., 2004; Measures, 1995; Pokrovsky & Schott, 2002b; Pokrovsky et al., 2010, 2015; Shiller & Bairamadgi, 2006; Shiller et al., 2006; Stoffyn & Mackenzie, 1982).



**Figure 5.** Schematic structures of Ga hydroxide complexes formed as a function of pH in aqueous solution during  $\text{Ga}^{3+}$  hydrolysis ( $[\text{Ga}(\text{aq})] = 10^{-3} \text{ M}$ ). After Pokrovski et al. (2002).



**Figure 6.** The adsorption of Ga(III) on goethite and calcite as a function of pH expressed as the percentage of Ga adsorbed in the experiment. (a) Goethite (10g/L; 84  $\text{m}^2/\text{g}$ ), modified from Persson et al. (2006), (b) Calcite (25 g/L, 18.6  $\text{m}^2/\text{g}$ ), Modified from Pokrovsky et al. (2004).

The flux of riverine Ga is a critical indicator of material transport from continent to ocean but remains poorly quantified. It is generally understood that concentrations of Ga and Al in river water are insignificant due to their quasi-insoluble nature resulting from a strong affinity with organic matter and preferential incorporation into secondary weathering products such as clay minerals (Shiller, 1988; Shiller & Frilot, 1996). Within the same basin, dissolved molar Ga/Al ratios are consistently higher than in solid materials (Table S8 and Figure 8). However, there is no apparent relationship between Ga and Al concentrations in solids and waters of a given river, implying that solid-phase Ga and Al are not key factors controlling their dissolved concentrations. Regarding carriers, studies of boreal river tributaries flowing to the White Sea, Russia, have shown that Ga and other insoluble trace metals are transported mainly (50%–80% in spring flood; 10%–40% in base-flow periods) as Fe-, Al-, and organic-rich colloids (Pokrovsky & Schott, 2002b; Pokrovsky et al., 2005, 2006, 2015; Vorobyev et al., 2019). Ultrafiltration (20%–90% in the 1 kDa 0.22  $\mu\text{m}$  size fraction) of boreal river water indicates no relationship between the concentration of colloidal Ga and seasonal hydrology changes or rock lithology in the basin; rather there seems to be a correlation between Ga and total-Fe and organic-carbon concentrations (Pokrovsky et al., 2010; Vasyukova et al., 2010).

In estuaries, Al and Ga concentrations are linearly correlated with salinity, with lower dissolved concentrations in less-saline waters (Orians & Bruland, 1985, 1988a, 1988b), interpreted as being due to strong adsorption of Ga and Al by particulate matter (Johnson, 2016; Kramer et al., 2004).

### 3.4.3. Gallium in the Ocean

As for many other elements, Ga in the ocean is derived mainly from continental fluvial and aeolian inputs, sediment-water interaction, hydrothermal input, and anthropogenic emissions (Bruland & Lohan, 2003; Chou & Wollast, 1997; Johnson, 2016; Orians & Bruland, 1988a, 1988b). Details of Ga geochemistry in the marine environment and its input fluxes are largely unknown. Dissolved Ga was recently used as a tracer to determine proportions of Pacific- and Atlantic-derived seawater in the Arctic Ocean, with water-source distributions being essentially equivalent to meteoric-water/sea-ice-melt fractions based on Ga as a conservative proxy in place of nutrients (Whitmore et al., 2020). Available data indicate that Ga concentrations in seawater are consistently higher than in river water. This may result from a combination of several factors including (a) sustained Ga input by weathering reactions (especially from continental Ga-rich phases such as mineral ores) and from anthropogenic sources, (b) marine processes such as dilution by seawater, adsorption of Ga onto marine sediments, and biological effects, and (c) loss of riverine Ga in the coastal zone due to changes in pH, salinity, and/or physicochemical and hydrodynamic conditions. The relative contributions of these factors are yet to be quantified (Orians & Bruland, 1988a; Shiller, 1988; Shiller & Frilot, 1996).

Since the first estimation of seawater Ga concentrations by spectrography over a century ago (Del Campo & Rodeja, 1914), sporadic measurements have been performed to constrain the Ga content in the ocean, particularly in the scope of comparison with Al (Hydes, 1979, 1983; Hydes & Liss, 1977; Measures & Edmond, 1988; Orians & Bruland, 1988a;

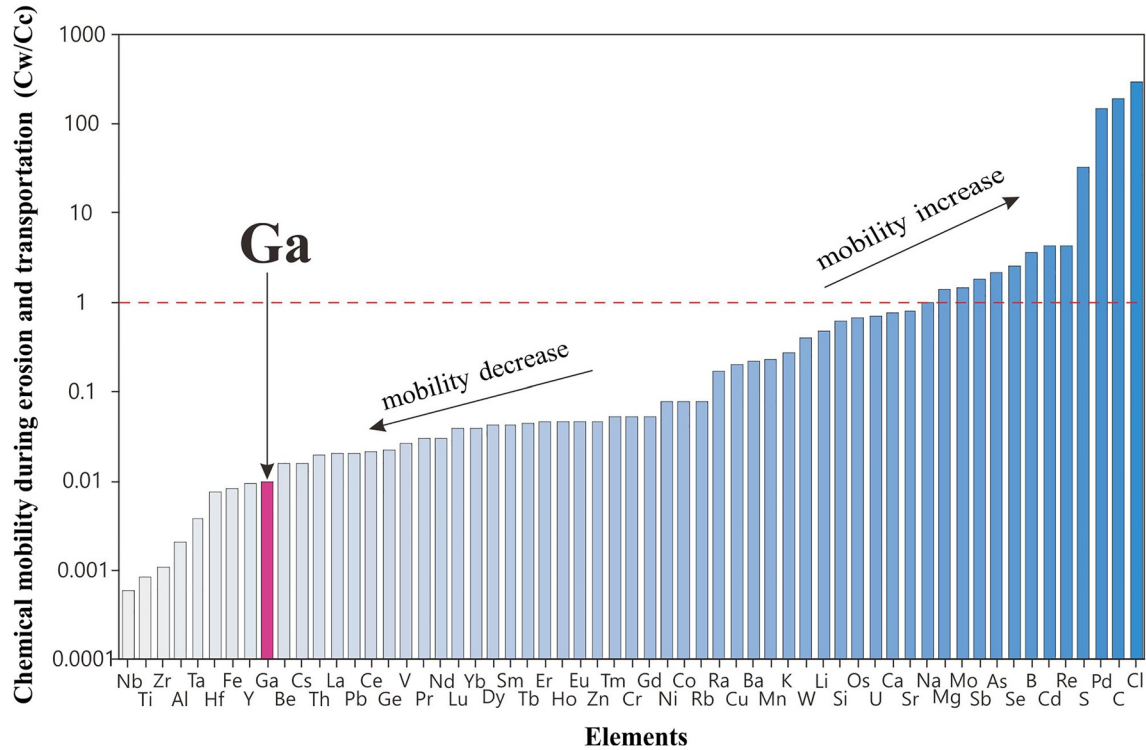


Figure 7. Chemical mobility of Ga (and other elements) relative to Na during surface weathering (Gaillardet et al., 2004).

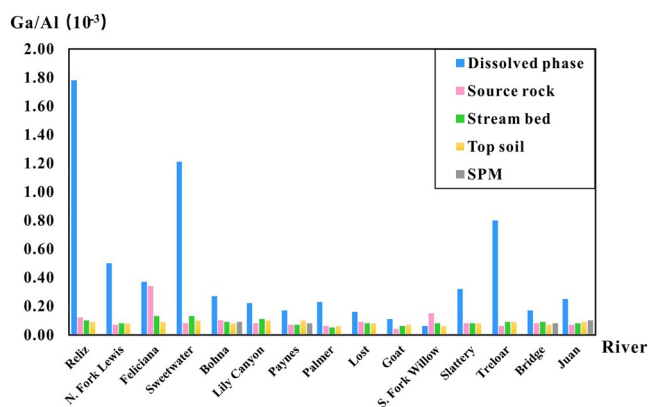
Pokrovski et al., 2002; Shiller, 1988; Shiller & Frilot, 1996). Water-column studies report a concentration range of 5–43 pmol kg<sup>-1</sup> in surface seawater (Table S4), with a minimum concentration at middepth, and an uptrend toward the sediment-water interface (Figure 9). Goldschmidt (1954) suggested that Ga may be enriched in seawater relative to Al, based on comparison with crustal sources. The Ga/Al ratio in both the Atlantic and Pacific oceans (Figure 9) is indeed over an order of magnitude higher than the corresponding crustal ratio. Seawater Al generally exhibits a similar trend with depth, although several studies have documented Ga geochemical behavior different to that of Al across the water column. This particular vertical distribution of Ga and Al may be caused by atmospheric deposition, organic-matter remineralization, scavenging by particles and colloids, or sediment-water interaction (Johnson, 2016; Orians & Bruland, 1988a, 1988b). For example, the rapid increase of Al at depth (>6,000 m) in some profiles may be explained by various possible mechanisms such as desorption from particle surfaces, release from decomposing biogenic carriers, and diffusion from sediments as inferred from the pore-water concentration gradient (Hydes, 1979; Orians & Bruland, 1985, 1988a, 1988b; Stoffyn-Egli, 1982), although these factors might impact differently on Ga concentration profiles.

Table 1  
Concentration of Ga and Al and Ga/Al Ratios in Various Aqueous Environments

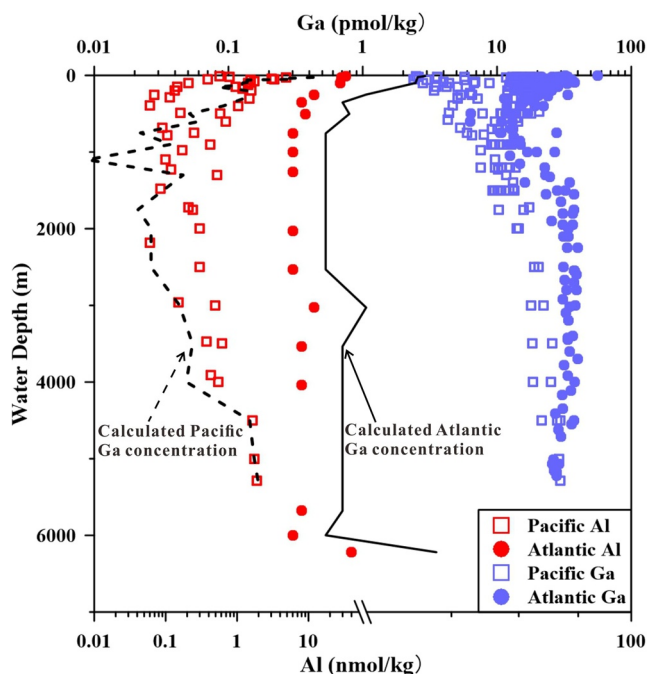
No.	Dissolved phase			Solid phase Ga (μg/g)				Solid phase Ga/Al × 10 <sup>-4</sup>			
	Ga (pmol//L)	Ga/Al × 10 <sup>-4</sup>	Al (nmol/L)	Source rock	Stream bed	Top soil	Susp. Sed.	Source rock	Stream bed	Top soil	Susp. Sed.
Californian streams	1–79	1.5–4.55	16–446	1.7–20	6.6–22	4.6–33	21–31	1.0–8.7	1.3–3.3	1.5–2.5	2.0–2.5
U.S. rivers	68–250	0.2–1.05	95–2370								
Thermal waters	2.9 × 10 <sup>4</sup> –3.6 × 10 <sup>5</sup>										

Note. The Ga/Al ratios is the mass ratios. Data taken from Goguel (1988), Shiller (1988), Shiller and Frilot (1996), Uzumasa and Nasu (1960), and Wood and Samson (2006).





**Figure 8.** Ga/Al mass ratio (in  $10^{-3}$  units) in different creeks in California (Shiller, 1988; Shiller & Frilot, 1996).



**Figure 9.** Dissolved Ga and Al concentration in depth-profiles of the Pacific and Atlantic oceans (Hydes, 1983; Orians & Bruland, 1986, 1988a, 1988b; Shiller & Bairamadgi, 2006; Shiller et al., 2006). The dashed line is the calculated Pacific Ga concentration estimated from the Ga/Al ratio of the upper continental crust (UCC) ( $0.0883, \text{pmol.kg}^{-1}/\text{nmol.kg}^{-1}$ , Hu & Gao, 2008; Rudnick & Gao, 2003) and the dissolved Pacific Al concentration ( $\text{nmol.kg}^{-1}$ , red square) of the same depth-profiles. The solid line is the calculated Atlantic Ga concentration with the data of UCC Ga/Al ratio and the dissolved Al concentration ( $\text{nmol.kg}^{-1}$ , red circle) of the same Atlantic depth-profiles.

Hydrothermal systems are another source of Ga in seawater, with Ga concentrations in geothermal waters being significantly higher than those in rivers and oceans albeit with a wide variation of 0.1–72 (Hydes, 1983; Orians & Bruland, 1986, 1988a, 1988b; Shiller & Bairamadgi, 2006; Shiller et al., 2006). The Ga content of geothermal sediments is particularly high, reaching 700 ppm (Goguel, 1988; Krupp & Seward, 1990; Riley, 2010; Shiller, 1988; Uzumasa & Nasu, 1960; Weissberg et al., 1979). However, the magnitude of the hydrothermal input flux of Ga to the oceans is not yet accurately constrained.

### 3.5. Gallium in the Biosphere

The relations between trace elements and lives are mutual. Trace elements are essential building materials for life, and biota regulate their transfer and transformation through metabolism and biogeochemical reactions, impacting their biogeochemical cycling. For Ga, however, its biological properties, occurrence in living organisms, physiological toxicity, and the effects of biota on its geochemical cycling are poorly understood. This preliminary review of the biochemical behavior of Ga may aid the evaluation of impacts of biota on Ga geochemical systematics in various environments.

The first study of Ga in biological samples was undertaken in 1919, when Cornec (1919) measured Ga concentrations in *Laminaria* sp. This was followed by determination of Ga concentrations in other marine organisms in 1935 (Vinogradov, 1935), and in oysters and human urine in 1941 (Bertrand, 1941). Follow-up studies detected the presence of Ga in various organisms, such as natural spices, seeds, fruits, and beetles, thus confirming the widespread occurrence of Ga in natural ecosystems (Bertrand, 1941; Cornec, 1919; Culkin & Riley, 1958b; Vinogradov, 1935). The concentration of Ga in most organisms is generally <1 ppm: *Squalus acanthias*, 0.1 ppm; body wall of *Asterias rubens* and *Bryssopsis lyrifera*, 0.7 ppm; and *Lycopodium flabelliforme* and *Mitchella repens*, 0.1–0.2 ppm (Bertrand, 1941; Culkin & Riley, 1958a; Hutchinson & Wollack, 1943; Ishiguro et al., 1952; Noddack, 1939). Culkin and Riley (1958a, 1958b) noted nonuniform distribution of Ga in a single organism, with significantly higher concentrations in viscera and digestive organs than other organs and tissues. Relatively high Ga concentrations of up to 60 ppm were determined in some lichens and bryophytes (Lounamaa, 1956; Shacklette, 1965). For microorganisms, Yamamoto et al. (1976) measured Ga concentrations in 30 different species of algae, finding a range from 0.02–0.64 ppm in dried samples (average 0.14 ppm). More importantly, the same study reported strong positive Ga-Al and Ga-Fe correlations in various seaweeds (Yamamoto et al., 1976). As seen in Table 2, Ga/Al ratios in marine organism range from  $1.2 \times 10^{-4}$  to  $7.2 \times 10^{-4}$ , similar to the average for upper continental crust (UCC) but generally lower than for Earth surface conditions (i.e., soils and surface waters). Relative to oceanic microorganisms, few data have been reported for Ga in continental plants, and there is no evidence that Ga is an essential micronutrient for crops and vegetables such as tomato, lettuce, and sugar beet (Culkin & Riley, 1958a, 1958b; Hewitt & Bolle-Jones, 1952). A wide range of Ga contents (0.02–60 ppm) have been reported for various continental plants, with relatively high concentrations in lichens and mosses (up to 60 and 30 ppm, respectively) for which the mecha-



**Table 2**  
Concentrations of Ga in Biological Materials

Species	Ga ( $\mu\text{g/g}$ )	Al ( $\mu\text{g/g}$ )	Ga/Al $\times 10^{-4}$	Reference
Marine plants				
Chlorophyceae Codiaceae	0.05–0.16	143–1,336	1.2–3.5	Culkin and Riley (1958a)
Phaeophyceae Fucaceae	0.01–0.10	34.4–372	2.7–7.2	Culkin and Riley (1958a)
Rhodophyceae Corallinaceae	0.23–0.56	94.8–4,420	1.3–4.0	Culkin and Riley (1958a)
<i>Lycopodium flabelliforme</i>	0.1			Hutchinson and Wollack (1943)
<i>Mitchella repens</i>	0.1–0.2			Hutchinson and Wollack (1943)
Marine animals				
<i>Squalus acanthias</i>	0.1			Burton et al. (1959)
<i>Asterias rubens</i> , <i>Bryssopsis lyrifera</i>	0.7			Burton et al. (1959)
Land plants				
Corn leaf	0.02–0.32		2.1–9.4	Prince (1957a, 1957b)
Lichen	0.02–60			Lounamaa (1956)
Bryophyte	up to 30		4.3	Shacklette (1965)

Note. The Ga/Al ratios is the mass ratios.

nisms of Ga incorporation remain unclear (Bowen, 1979; Dvornikov et al., 1976; Gribovskaya et al., 1968; Kabata-Pendias, 2010; Lounamaa, 1956; Poledniok, 2008; Shacklette et al., 1978; Shacklette, 1965; Steinberg, 1938, 1939a, 1939b, 1941; Wedepohl, 1969).

It is well known that heavy metals can lead to tissue damage when their intake exceeds certain limits (Liu et al., 2019), harming organism growth and even posing a threat to life. For Ga, however, median lethal doses ( $LD_{50}$ ), and comprehensive understanding of morphological transformation, *in vivo* migration, and physiological effects on various organisms have yet to be established (Maghakyan et al., 2017). Available  $LC_{50}$  data for Ga for different aquatic organisms (Table 3) indicate that high Ga concentrations in the aquatic environment may pose a threat to life therein. Furthermore, even in a diluted environment, Ga may be harmful to the health and life of certain organisms with long exposures. The  $LC_{50}$  of Ga is sensitive to the salinity of aqueous solutions, as they display an excellent positive correlation, similar to the relationship between salinity and  $LC_{50}$  for Zn and Ca (Blackmore & Wang, 2003; Burke et al., 2003; Hall & Anderson, 1995; Lin & Dunson, 1993; Onikura et al., 2005; Voyer & Modica, 1990). Early experimental results indicate that the asymptotic maximum Ga concentration is 2 mg kg  $DM^{-1}$  (DM, dry matter) in wheat tops and 18 mg kg  $DM^{-1}$  in wheat roots, much higher than those of other elements such as B, La, Fe, and Cu under the same conditions. Such a high rate of Ga consumption poses a hazard to the physical health of wheat (Wheeler & Power, 1995).

Apart from elemental Ga, the wide application of high-purity As compounds in the semiconductor industry and ensuing waste products such as computer circuitboards and photodiodes calls for attention to the physiological toxicity of artificial Ga-bearing compounds such as GaAs (Dupuis, 1984; Robinson, 1983; Tanaka, 2004). Strong evidence has been presented that GaAs is not only a toxin that directly damages the lungs and reproductive organs of animals but also a human carcinogen. The chronic physiological toxicity of GaAs is not entirely clear but is of environmental concern because of its aqueous solubility (Program, 2000; Rosner & Carter, 1987; Webb et al., 1984; Yamauchi et al., 1992). Due to

**Table 3**  
The  $LC_{50}$  of Ga of Different Aquatic Organisms

Species	Exposure periods	$LC_{50}$ (mg/L)	Reference
<i>Americamysis bahia</i>	24 h	22.47	Onikura et al. (2005)
<i>Americamysis bahia</i>	96 h	12.76	
<i>Brachionus plicatilis</i>	24 h	11.48	
<i>Artemia salina</i>	24 h	54.64	
<i>Artemia salina</i>	48 h	52.78	
<i>Danio rerio</i>	48 h	17.70	Yang and Chen (2018)
<i>Danio rerio</i>	72 h	12.18	
<i>Danio rerio</i>	96 h	9.10	
<i>Rhodeus ocellatue</i>	48 h	18.02	
<i>Rhodeus ocellatue</i>	72 h	14.54	
<i>Rhodeus ocellatue</i>	96 h	10.71	
<i>Cyprinus carpio</i>	48 h	28.81	
<i>Cyprinus carpio</i>	72 h	22.11	
<i>Cyprinus carpio</i>	96 h	19.78	Yang and Chen (2003)

**Table 4**  
Masses of Ga in Earth Reservoirs

Reservoirs	The masses of Ga (t)
Earth core	$(4.5 \pm 3.6) \times 10^{15} / (9.9 \pm 4.3) \times 10^{15}$
Earth mantle	$1.6 \times 10^{16}$
Earth crust	$5.07 \times 10^{14}$
SOC	$2.1 \times 10^{15}$
Lithosphere	$10^{15}$
Soils	$8.5 \times 10^{10}$
Ocean	$1.6 \times 10^6$

the increasing demand for electronic products, the use of Ga is expected to grow rapidly, making the study of its environmental effects and physiological toxicity a matter of urgency.

However, it is known that Ga is a beneficial element for the growth of certain microorganisms and fungi such as *Aspergillus Niger* and duckweed *Lemna minor*. It is also the only element that competes with Fe for entry to organisms through membranes (Culkin & Riley, 1958a, 1958b; Emery & Hoffer, 1980; Gascoyne et al., 1991; Shiller, 1988). Few studies have explored the physiological effects of Ga. Riley (1943) reported that in nutrient-deficient cultures the growth of the marine diatom, *Nitzschia closterium*, was stimulated by Ga, but this effect disappeared in the presence of nitrate and phosphate (Culkin & Riley, 1958a, 1958b). Hutchinson and Wollack (1943) found that Ga, as gallous and gallic salts or cyanide complexes, has a greater re-

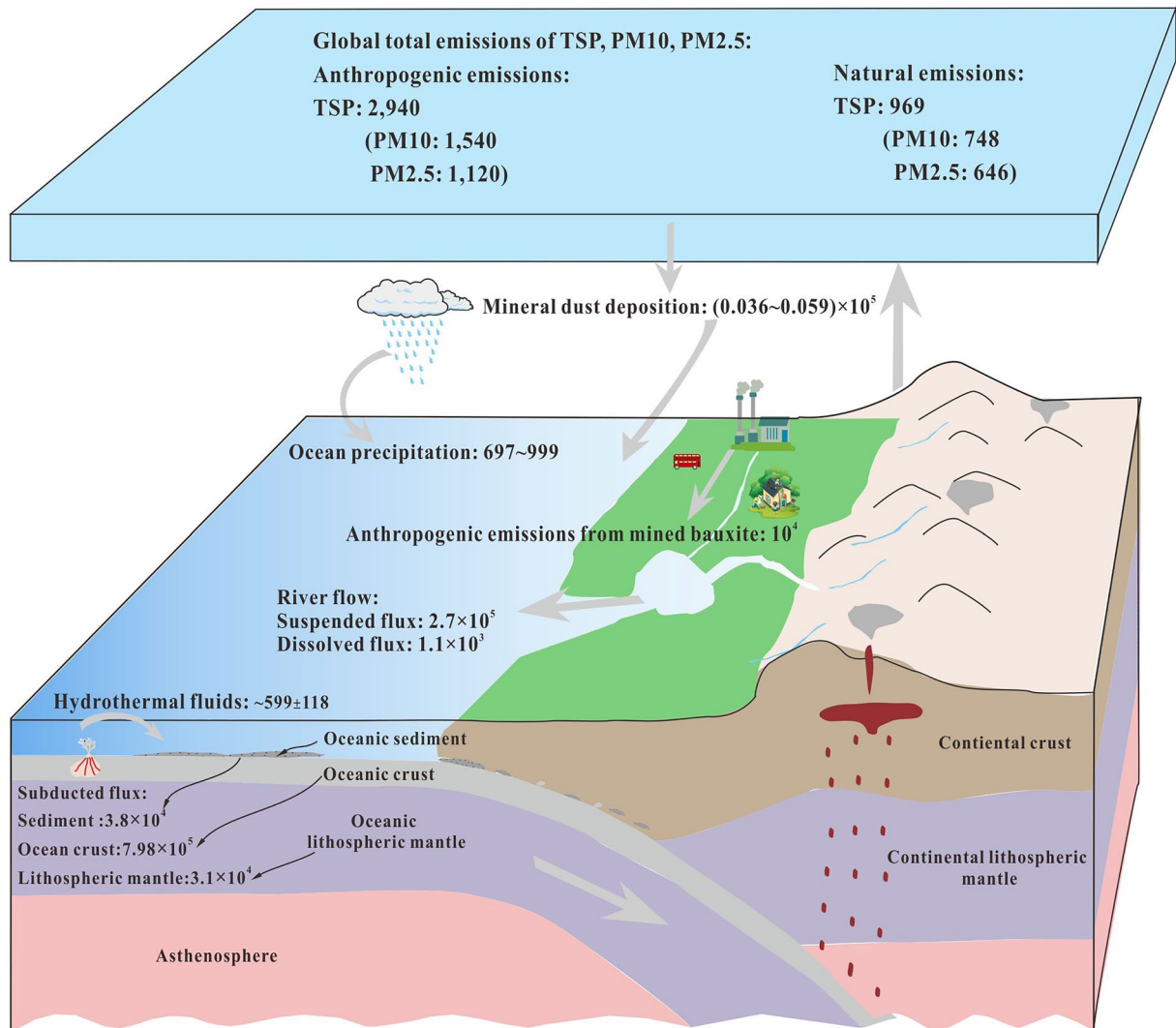
semblance to Fe than Al in many biological respects (Culkin & Riley, 1958a, 1958b). These older studies pioneered the investigation of Ga biogeochemistry but did not probe the underlying mechanisms responsible for any physiological benefit of Ga. However, recent data began to unveil pathways, for example, trace Ga has been used in the treatment of Kashin Beck disease for Ca fixation, and its radioactive isotopes have been used for diagnostic and therapeutic purposes (Liu et al., 2016; Matkovic et al., 1990).

### 3.6. The Global Biogeochemical Cycle of Ga

No reconstruction of the global biogeochemical cycle of Ga has been reported to date, so we made a tentative effort to conceptualize a model of global Ga cycling based on published data for Ga storage in different geological reservoirs (Table 4) and relative trans-reservoir fluxes (Figure 10), with a focus on the oceanic Ga budget. Volcanism is not included in the model because although a potentially important natural source, it is not yet possible to estimate volcanic Ga emissions owing to a lack of data and uncertainties in characterizing volcanic eruptions (e.g., ash particle size distribution). However, our model does include estimated anthropogenic Ga releases to the environment.

A number of considerations are factored into the model, as follows.

1. Løvik et al. (2015) found that Ga recovery from bauxite (its main geogenic source) leads to a Ga exploitation flux of  $\sim 11,000$  tonnes (t)  $\text{yr}^{-1}$ , of which  $< 300$  t  $\text{yr}^{-1}$  is utilized in primary and secondary products, with the remainder (in red mud) entering the Al cycle as an impurity.
2. The anthropogenic flux of Ga to the atmosphere was calculated from aerosol Ga contents and emissions. Huang et al. (2014) estimated that in 2007 the average global emission of total suspended particulates (TSP),  $\text{PM}_{10}$  (particles  $\leq 10 \mu\text{m}$  diameter), and  $\text{PM}_{2.5}$  ( $\leq 2.5 \mu\text{m}$ ) were  $162 \times 10^6$ ,  $99 \times 10^6$ , and  $78 \times 10^6$  t, to which anthropogenic sources contributed  $105 \times 10^6$ ,  $55 \times 10^6$ , and  $40 \times 10^6$  t, respectively. As no data exist specifically for anthropogenic aerosol, the average Ga content of  $\sim 28$  ppm for  $\text{PM}_{2.5}$  measured recently in Beijing (September 15 to October 16, 2015; unpublished data) was applied. The crustal abundance of  $\sim 17$  ppm was applied as the Ga content of natural aerosol (Burton et al., 1959). Gallium fluxes to the atmosphere carried by TSP,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$  are thus of the order of 3,909, 2,288, and 1,766 t  $\text{yr}^{-1}$ , of which anthropogenic emissions account for about 2,940, 1,540, and 1,120 t  $\text{yr}^{-1}$ , and natural sources about 969, 748, and 646 t  $\text{yr}^{-1}$ , respectively. The flux of Ga to the atmosphere carried by anthropogenic and natural  $\text{PM}_{10}$  particles thus constitutes 52% and 77% of anthropogenic TSP, respectively, to which  $\text{PM}_{2.5}$  contributes more than 70% (72% and 86% for anthropogenic and natural  $\text{PM}_{10}$ , respectively). The relatively high Ga content in fine particles means a prolonged higher level in the atmosphere, although the actual aerosol residence time was not considered here due to the lack of relevant data.
3. There are numerous sources of Ga flux to oceans and each must be evaluated. (a) Atmospheric dust deposition to oceans is of the order of  $5.3 \times 10^8$ – $8.5 \times 10^8$  t  $\text{yr}^{-1}$  globally, including 8 wt.% Al (Maring & Duce, 1987). Of the total Al deposition, it is estimated that 9% is released into seawater by dissolution, implying  $3.8 \times 10^6$ – $6.1 \times 10^6$  t  $\text{yr}^{-1}$  dissolved Al and  $3.8 \times 10^7$ – $6.1 \times 10^7$  t  $\text{yr}^{-1}$  particulate Al are supplied annually to the oceans by dust deposition (Maring & Duce, 1987). Based on the UCC Ga/Al ratio of



**Figure 10.** The global Ga flux (unit:  $\text{t yr}^{-1}$ ). Data from Al-Khatib et al. (2019); Bruland (1983); Evans (2012); Gale et al. (2013); Hu and Gao (2008); Huang et al. (2014); Hunt (1972); Koljonen (1992); Løvik et al. (2015); Li (1985); Lodders and Fegley (1998); Maring and Duce (1987); Matschullat (2000); Metz and Trefry (2000); Nielsen et al. (2006); Niu et al. (2012); O'Neill and Palme (1998); Prospero (1981); Rudnick and Gao (2003); Trenberth et al. (2007); Viers et al. (2009).

$0.0883 \text{ pmol kg}^{-1}/\text{nmol kg}^{-1}$ ,  $330\text{--}540 \text{ t yr}^{-1}$  of dissolved and  $3,300\text{--}5,400 \text{ t yr}^{-1}$  of particulate Ga are delivered as mineral dust to the oceans (Hu & Gao, 2008; Maring & Duce, 1987; Prospero, 1981; Rudnick & Gao, 2003). However, considering the different residence times of Ga and Al in the ocean ( $\sim 750$  and 150 years, respectively; Orians & Bruland, 1988a, 1988b; Shiller, 1998), this estimate based on the crustal Ga/Al ratio should be considered with caution. (b) Rainwater is another source of oceanic Ga. The Ga content of rainwater varies from  $0.51$  to  $42.2 \mu\text{g L}^{-1}$  in different continental areas, with means of  $1.9\text{--}2.7 \mu\text{g L}^{-1}$  (Al-Khatib et al., 2019). Considering an estimated  $373 \text{ Tt yr}^{-1}$  total precipitation over the global ocean (Trenberth et al., 2007),  $700\text{--}1,000 \text{ Ga t yr}^{-1}$  are deposited. (c) The flux of Ga from continent to ocean in suspended phases of rivers and hydrothermal fluids must also be considered. A suspended-sediment flux of  $272 \times 10^3 \text{ t yr}^{-1}$  was estimated on the basis of a global sediment flux of  $15 \text{ Gt yr}^{-1}$  with an average Ga content of  $18.1 \text{ ppm}$  (Viers et al., 2009). Similarly, the dissolved Ga flux from rivers to oceans is about  $1.1 \times 10^3 \text{ t yr}^{-1}$  (Gaillardet et al., 2003, 2014; Viers et al., 2009). However, this dissolved Ga flux may be overestimated, as the recent studies report much lower Ga contents in riverwaters (Colombo et al., 2019; Gaillardet et al., 2014; Shiller & Frilot, 1996; Whitmore, et al., 2020), and the riverine dissolved Ga may be further partially scavenged and removed by complex processes at

estuary (Ho et al., 2019; Mcalister & Orians, 2012; Schier et al., 2021). To be mentioned, the delivery of sediments to oceans most likely increases with time, implying a change in the continental Ga flux over geological history (Vanlaningham et al., 2009), although the historical Ga-ocean flux is beyond the scope of this study. (d) Fluxes of high-temperature hydrothermal water flux of  $5.6 \pm 0.6 \times 10^{10} \text{ t yr}^{-1}$  (German & Seyfried, 2014), with corresponding Ga contents of 25–67 nmol kg<sup>-1</sup> (Metz & Trefry, 2000; Nielsen et al., 2006) provide estimated hydrothermal inputs of Ga to the oceans of 98–265 t yr<sup>-1</sup>. Ho et al. (2019) estimate a much higher global dissolved Ga flux from hydrothermal activity of  $599 \pm 118 \text{ t yr}^{-1}$  using the slope of the Ga-<sup>3</sup>He<sub>ex</sub> linear regression and the global <sup>3</sup>He hydrothermal flux (Ho et al., 2019).

4. The subduction-induced flux of Ga from the ocean floor to Earth's interior must also be considered. The total fluxes of subducted sediments, oceanic crust, and lithospheric mantle are 1.7, 45.6, and 13 Gt yr<sup>-1</sup>, respectively (Evans, 2012). Considering typical Ga contents of marine sediments (22 ppm), MORB (17.5 ppm), and spinel-peridotite xenoliths (2.4 ppm), considered here as representing deep lithosphere; Burton et al., 1959; Gale et al., 2013; McDonough, 1990a), total subducted Ga fluxes are estimated to be  $3.8 \times 10^4 \text{ t yr}^{-1}$  for marine sediment,  $8 \times 10^5 \text{ t yr}^{-1}$  for oceanic crust, and  $3.1 \times 10^4 \text{ t yr}^{-1}$  for lithospheric mantle. However, the true outflux of Ga from the oceans may be close to  $3.8 \times 10^4 \text{ t}$ , as most Ga in oceanic crust and lithospheric mantle derived from ridge uplift would not participate in oceanic cycling (Orians & Bruland, 1988a, 1988b).

Collectively, the oceanic Ga budget is driven by  $3.2\text{--}16.2 \times 10^5 \text{ t yr}^{-1}$  inputs, including 0.7–0.9 kt yr<sup>-1</sup> from precipitation, 3.6–5.9 kt yr<sup>-1</sup> from dust deposition, up to  $599 \pm 118 \text{ t yr}^{-1}$  from hydrothermal fluids, and 0.3 Mt yr<sup>-1</sup> from rivers. Rivers and hydrothermal fluids are thus the main contributors of Ga to the oceans, with the total influx being higher than the total Ga outflux associated with subduction. We emphasize that, because of the lack of data, these assessments are first-order approximations only, and more systematic studies of, for example, the range of Ga concentrations in hydrothermal and geological samples and the residence time of Ga in the ocean, are needed to reduce uncertainties.

We now turn to the estimate of Ga storage in various Earth reservoirs. We consider the mantle, lithosphere, pedosphere, ocean, and subducted oceanic crust (SOC, a pivotal reservoir for transport of surface materials to the deep Earth; Table 4). (a) Based on the Ga contents of the various spheres of the solid Earth discussed above, the corresponding masses of Ga in the core, mantle, and crust are estimated to be  $4.5 \pm 3.6 \text{ Pt}$  or  $9.9 \pm 4.3 \text{ Pt}$ , 16 Pt, and 0.5 Pt, based on compartment masses of 1.9 Zt, 4 Zt, and 0.03 Zt, respectively (Burton et al., 1959; Lodders & Fegley, 1998; O'Neill & Palme, 1998). (b) The lithosphere provides almost all Ga resources to surface reservoirs including soil, biota, and even humans. Gallium storage in the lithosphere is  $\sim 1 \text{ Pt}$ , based on the mass of the lithosphere (124 Et) and its average Ga content of 8.7 ppm (Li, 1985). (c) The total global mass of soils is about 1/25,000 that of the lithosphere (i.e., 5 Pt; Matschullat, 2000), so 85 Gt of Ga is estimated to be stored in soils globally, based on a mean content of 17 ppm (Burton et al., 1959; Koljonen, 1992; Matschullat, 2000). (d) The global ocean stores a total of  $\sim 1.6 \text{ Mt}$  Ga, based on an ocean mass of 1.4 Et and the average oceanic Ga concentration of 17 pmol kg<sup>-1</sup> (Bruland, 1983). (e) With regard to the SOC, assuming it constitutes  $\sim 3 \text{ wt}\%$  of the entire mantle (4 Zt), its mass would be about 0.1 Zt (Gale et al., 2013; Niu et al., 2012). Using the Ga content of MORB for SOC, the total SOC Ga mass is about 2 Pt. (f) Estimation of the total Ga content of the atmosphere is not yet possible due to a lack of data, particularly concerning variations in particle size and type, and of deposition between different regions.

#### 4. The Isotopic Geochemistry of Ga

Gallium has a total of 26 radioactive isotopes and two stable isotopes (<sup>69</sup>Ga and <sup>71</sup>Ga; Gross & Thoennessen, 2012; Laeter, 1972). All radioactive Ga isotopes have half-lives of <80 h and are often used in nuclear medicine applications (Gross & Thoennessen, 2012). This section is devoted entirely to the stable isotopic geochemistry of Ga.

The abundances of <sup>69</sup>Ga and <sup>71</sup>Ga are 60.1% and 39.9%, respectively (Laeter, 1972). Gallium isotopic compositions are normally expressed as  $\delta^{71}\text{Ga}$ , in per mil units:

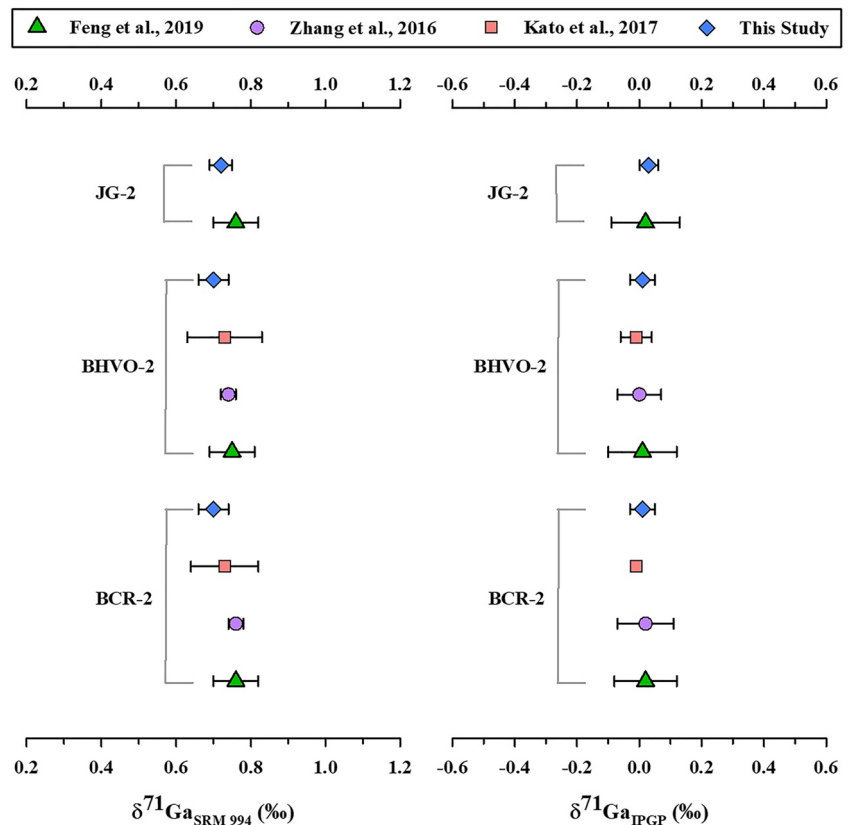
$$\delta^{71}\text{Ga} = \left[ \left( \frac{{}^{71}\text{Ga}/{}^{69}\text{Ga}}{\text{sample}} \right) / \left( \frac{{}^{71}\text{Ga}/{}^{69}\text{Ga}}{\text{standard}} \right) - 1 \right] \times 1000 \quad (1)$$

Here, the standard is the US National Institute of Standards and Technology (NIST) standard reference material (SRM) 994 solid metal Ga ( $\text{Ga}^{69/71} = 1.50676 \pm 0.00039$ , at the 95% confidence level; Machlan et al., 1986; Yang & Meija, 2010; Yuan et al., 2016; Zhang et al., 2016). Alternative standards have been used as reference materials in other Ga isotope studies (Kato & Moynier, 2017a, 2017b; Kato et al., 2017; Zhang et al., 2016).

Gallium isotopic compositions were first determined more than 70 years ago when Inghram et al. (1948) found no significant difference in isotopic ratios between terrestrial and meteoritic materials, most likely because of a lack of sufficient precision. Laeter (1972) then determined Ga isotopic compositions of meteorites, but with uncertainties as high as 1.1‰. Since then, there have been a number of attempts to develop better analytical methods, such as purifying Ga from geological samples using chromatographic techniques with different ion-exchange resins and acids (Dembiński et al., 2006; Kiriyama & Kuroda, 1988; Machlan & Gramlich, 1988). However, the accurate determination of Ga isotopic composition remained elusive, due either to incomplete recovery of Ga or to significant isotopic fractionation during chromatographic elution, with the heavier isotope having a stronger affinity for the resins (e.g., Dowex 50-X8 resin and AG 1 × 4 resin) than the lighter isotope (Dembiński et al., 2006; Machlan & Gramlich, 1988). Sample purification, together with instrumental limitations for determining Ga isotopic ratios, became the rate-limiting step in the investigation of Ga isotopic geochemistry for about three decades. It was not until 2016 when three chromatographic purification methods were established simultaneously, allowing more accurate analysis of Ga isotopic compositions based on MC-ICP-MS instrumentation (Kato et al., 2017; Yuan et al., 2016; Zhang et al., 2016). Data precisions of better than 0.06‰ (2SD), with a variation in  $\delta^{71}\text{Ga}$  values of up to 1.83‰ across different industrial and natural materials were achieved, opening the way for Ga isotopic approaches in various research studies. However, studies using the different purification methods reported inconsistent  $\delta^{71}\text{Ga}$  values for certain reference materials (Feng et al., 2019; Kato et al., 2017; Wimpenny et al., 2020; Yuan et al., 2016; Zhang et al., 2016), requiring further study of technique reliability. We performed an international calibration and comparison of  $\delta^{71}\text{Ga}$  values for set reference materials, with results indicating that  $\delta^{71}\text{Ga}$  values, relative to both the NIST SRM 994 and IPGP-Ga standard (Feng et al., 2019; Kato et al., 2017; Yuan et al., 2016; Zhang et al., 2016), of our newly purchased reference materials JG-2, BHVO-2, and BCR-2 were consistent with those reported previously by other laboratories (Figures 11 and 12, Table S9). Inter-laboratory and international calibration of standards should thus be undertaken regularly to test method reliability and to evaluate possible standard heterogeneity or contamination (Feng et al., 2019; Kato et al., 2017; Wimpenny et al., 2020; Yuan et al., 2016; Zhang et al., 2016).

The implications of Ga isotopic composition are not yet fully resolved; however, preliminary studies have clearly shown the interest of Ga isotopes to geoscience research. Cosmochemically, volatilization significantly fractionates isotopes of volatile elements such as Hg, B, Zn, Cu, and Sn (Bouchard et al., 2008; Creech & Moynier, 2019; Luck et al., 2005; Paniello et al., 2012; Xiao et al., 1997; Zheng et al., 2007), and the recently developed Ga isotopic approach may provide a powerful alternative in the study of processes involved in the loss of volatile elements from planetary bodies (e.g., chondrites, the Moon, and CAIs). For example, Ga isotopes have been used to study the origin of volatiles depletion in primitive meteorites (Kato & Moynier, 2017a). The observed enrichment of the heavier Ga isotope in the most volatiles-rich meteorites (CI chondrites) likely indicates that the Ga budget of the parent bodies of primitive chondrites was not controlled by evaporation within the Solar System, but rather was inherited from very early nebular processes (Figure 12; Kato & Moynier, 2017a). A recent study has shown that CAIs are enriched in the light Ga isotope, with Ga isotopes thus being of interest in identifying the fate of moderately volatile elements in planetary bodies and refractory inclusions (Kato & Moynier, 2017b). Furthermore, bulk primitive meteorites, most likely the building blocks of terrestrial planets, exhibit variable  $\delta^{71}\text{Ga}$  values (by ~1‰) negatively correlated with Al/Ga ratios, as observed similarly for other moderately volatile elements such as Zn (Pringle et al., 2017) and Rb (Pringle & Moynier, 2017), suggesting a lack of evaporation effect in the volatile-element budget. Through analysis of a series of terrestrial mafic and ultra-mafic rocks (ocean-island basalts, MORBs, and komatiites), Kato and Moynier (2017a) found that Ga isotopes are not significantly

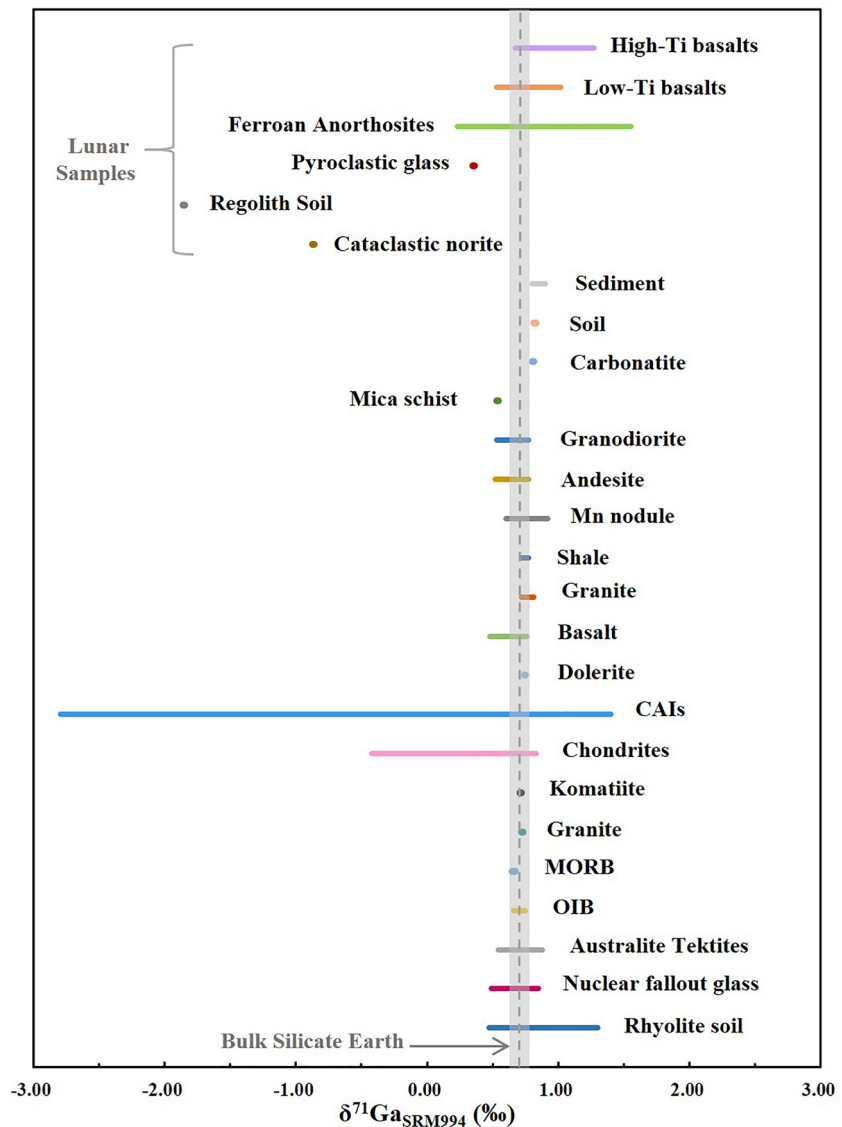




**Figure 11.**  $\delta^{71}\text{Ga}$  values for geological reference materials, normalized to NIST SRM 994 (a) and IGP Ga standard (b), respectively (see detailed in Table S9). Data from Feng et al., 2019 (green triangle); Kato et al., 2017 (red box), and Zhang et al., 2016 (purple circle) are also displayed. Blue diamonds are the  $\delta^{71}\text{Ga}$  values measured in this study.

fractionated during magmatic differentiation and have an average bulk silicate Earth isotopic composition of  $\delta^{71}\text{Ga} = \sim 0.00\text{‰} \pm 0.06\text{‰}$  (relative to the IGP-Ga; Figure 12; Table S9).

Another promising potential application of Ga isotopes is the investigation of surface weathering processes, with Ga being an analog of Al, a major component of aluminosilicates commonly considered conservative during surface alteration (Hydes, 1979; Hydes & Liss, 1977; Measures & Edmond, 1988; Orians & Bru-land, 1988a, 1988b; Pokrovsky & Schott, 2002a; Richardson & Derry, 2016; Shiller & Frilot, 1996). Previous studies have shown that isotopes of elements such as Mg, Ca, Ba, and Li are powerful tools in investigating surface weathering and its relative climatic and environmental effects (Dellinger et al., 2014; Gussone et al., 2016; Hindshaw et al., 2011; Opfergelt et al., 2012; Teng et al., 2010; Tipper et al., 2006), but none of these act as a reliable proxy for trivalent Al. Yuan et al. (2016) studied the adsorption of Ga on surfaces of calcite and goethite minerals, and found significant Ga isotopic fractionation (up to 1.3‰) during Ga adsorption (Yuan et al., 2018), foreshadowing the potential application of Ga isotopes in tracing and characterizing surface biogeochemical processes. Previous studies have also reported that industrially produced Ga materials are significantly enriched in the heavy isotope relative to geological materials, foretelling the usefulness of Ga isotopes for distinguishing natural from anthropogenic sources (Feng et al., 2019; Kato et al., 2017; Yuan et al., 2016; Zhang et al., 2016). It is thus safe to conclude that Ga isotopes are likely to provide additional clues concerning yet-underconstrained Al behavior and its biogeochemical cycle, and shed new light on other biogeochemical processes in which Ga is involved.



**Figure 12.**  $\delta^{71}\text{Ga}$  values (normalized to NIST SRM 994 Ga standard) in different natural samples. Data derived from this study and taken from Feng et al. (2019), Kato et al. (2017), Wimpenny et al. (2020), Yuan et al. (2016), and Zhang et al. (2016). The Ga isotopic composition of Bulk Silicate Earth (BSE) was obtained from Kato et al. (2017).

## 5. Conclusions and Geochemical Implications

More than a century of research on the systematics of Ga in various Earth reservoirs has provided a large data set that significantly improves knowledge of Ga biogeochemistry. Recently developed isotopic approaches will undoubtedly be useful in tracing the origin of Ga and elucidating the geological and biological processes that modify its fate in Earth systems. This review is a compilation of available published data and provides a state-of-the-art view of the geochemistry of Ga and related applications.

This review also highlights major knowledge gaps in Ga systematics, including the lack of data for deep Earth reservoirs, the behavior of Ga during surface weathering, the transfer and transformation of Ga in surface ecosystems, the coupling of Ga with Al, Fe, and other elements such as Ge, B even Zn, the relationship between Ga and biota and its effect on the global Ga biogeochemical cycle, and the biological properties of Ga and its derivatives and their possible physiological toxicity. Attention to these areas has the potential to shape future research in this field.

An emerging need is a mechanistic view of processes responsible for Ga isotopic fractionation and applications of Ga isotopic composition. Future progress in this aspect may improve our understanding of the global biogeochemical cycling of terrestrial Ga. Cosmochemically, as volatilization significantly fractionates isotopes of volatile elements, a Ga isotope approach may provide an effective tool in improving our understanding of processes triggering the depletion of volatile elements in planetary bodies (e.g., chondrites, the Moon, and CAIs) and the Solar System evolution.

## Data Availability Statement

Data of Ga, Ni, and Ge concentrations in the classification of iron meteorites are available through Campbell and Humayun (2005), Choi et al. (1995), Cobb and Moran (1965), Lovering et al. (1957), Wasson and Kallemeyn (2002), Wasson and Richardson (2001), Wasson (1999), Wasson and Choe (2009), and Wasson et al. (2007). Data of the concentration of Ga and Al and Ga/Al ratio in various aqueous environments are available through Goguel (1988), Shiller (1988), Shiller and Frilot (1996), Uzumasa and Nasu (1960), and Wood and Samson (2006). Data from gallium concentrations in representative minerals and rocks are available through <http://georoc.mpch-mainz.gwdg.de/georoc> (Georock database on January 1, 2021).

## Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (41625012, 41973007, U1612442, 41961144028, 41830647) and the National Key R&D Program of China (2019YFC1804400). We appreciate two anonymous reviewers for insightful and critical comments, and Peter Raymond for careful and efficient editorial handling.

## References

- Ahrens, L. H. (1954). The lognormal distribution of the elements. *Geochimica et Cosmochimica Acta*, 6(2–3), 121–131. [https://doi.org/10.1016/0016-7037\(54\)90021-6](https://doi.org/10.1016/0016-7037(54)90021-6)
- Ahrens, L. H. (1964). The significance of the chemical bond for controlling the geochemical distribution of the elements. *Physics and Chemistry of the Earth*, 5, 1–54. [https://doi.org/10.1016/s0079-1946\(64\)80002-1](https://doi.org/10.1016/s0079-1946(64)80002-1)
- Akaiwa, H. (1966). Abundances of selenium, tellurium, and indium in meteorites. *Journal of Geophysical Research*, 71(7), 1919–1923. <https://doi.org/10.1029/jz071i007p01919>
- Albarède, F. (2009). Volatile accretion history of the terrestrial planets and dynamic implications. *Nature*, 461(7268), 1227–1233. <https://doi.org/10.1038/nature08477>
- Alina, K.-P. (2010). Chapter 18. Elements of Group 13. In *Trace elements in soils and plants* (4th ed., pp. 315–332).
- Al-Khatib, I. A., Arafeh, G. A., Al-Qutob, M., Jodeh, S., Hasan, A., Jodeh, D., & van der Valk, M. (2019). Health risk associated with some trace and some heavy metals content of harvested rainwater in Yatta area, Palestine. *Water*, 11(2), 238. <https://doi.org/10.3390/w11020238>
- Allen, R. O., & Mason, B. (1973). Minor and trace elements in some meteoritic minerals. *Geochimica et Cosmochimica Acta*, 37(6), 1435–1456. [https://doi.org/10.1016/0016-7037\(73\)90081-1](https://doi.org/10.1016/0016-7037(73)90081-1)
- Anbar, A. D., Roe, J. E., Barling, J., & Neelson, K. H. (2000). Nonbiological fractionation of iron isotopes. *Science*, 288(5463), 126–128. <https://doi.org/10.1126/science.288.5463.126>
- Baedecker, P. A., & Wasson, J. T. (1970). Ga, Ge, In, Ir and Au in lunar, terrestrial and meteoritic basalts. *Geochimica et Cosmochimica Acta*, 2.
- Balistreri, L. S., Box, S. E., & Tonkin, J. W. (2003). Modeling precipitation and sorption of elements during mixing of river water and porewater in the Coeur d'Alene River basin. *Environmental Science & Technology*, 37(20), 4694–4701. <https://doi.org/10.1021/es0303283>
- Benézeth, P., Diakonov, I. I., Pokrovski, G. S., Dandurand, J. L., Schott, J., & Khodakovskiy, I. L. (1997). Gallium speciation in aqueous solution. Experimental study and modelling: Part 2. Solubility of  $\alpha$ -GaOOH in acidic solutions from 150 to 250°C and hydrolysis constants of gallium (III) to 300°C. *Geochimica et Cosmochimica Acta*, 61(7), 1345–1357. [https://doi.org/10.1016/s0016-7037\(97\)00012-4](https://doi.org/10.1016/s0016-7037(97)00012-4)
- Bennett, R., & Czechowski, F. (1980). Gallium porphyrins in bituminous coal. *Nature*, 283(5746), 465–467. <https://doi.org/10.1038/283465a0>
- Bertrand, D. (1941). Importance of the trace element vanadium for *Aspergillus Niger*. *Comptes rendus de l'Académie des Sciences*, 213, 254–257.
- Bidelman, W. P., & Corliss, C. H. (1962). Identification of GA II Lines in Stellar Spectra. *The Astrophysical Journal*, 135(3), 968. <https://doi.org/10.1086/147341>
- Bischoff, A., Palme, H., & Spettel, B. (1987). A37—A coarse-grained, volatile element-poor Ca, Al-rich inclusion with huge Fremdlinge (Vol. 18).
- Blackmore, G., & Wang, W. X. (2003). Inter-population differences in Cd, Cr, Se, and Zn accumulation by the green mussel *Perna viridis* acclimated at different salinities. *Aquatic Toxicology*, 62(3), 205–218. [https://doi.org/10.1016/s0166-445x\(02\)00083-8](https://doi.org/10.1016/s0166-445x(02)00083-8)
- Blakemore, J., Schultz, J., & Myers, J. (1962). Measurements on gallium-doped germanium thermometers. *Review of Scientific Instruments*, 33(5), 545–550. <https://doi.org/10.1063/1.1717914>
- Blanchard, I., Badro, J., Siebert, J., & Ryerson, F. J. (2015). Composition of the core from gallium metal–silicate partitioning experiments. *Earth and Planetary Science Letters*, 427, 191–201. <https://doi.org/10.1016/j.epsl.2015.06.063>
- Borislenok, L., & Saukov, A. (1960). Geochemical cycle of gallium. In *International Geological Congress Report 21st Session* (pp. 96–105).
- Bouchard, D., Höhener, P., & Hunkeler, D. (2008). Carbon isotope fractionation during volatilization of petroleum hydrocarbons and diffusion across a porous medium: A column experiment. *Environmental Science & Technology*, 42(21), 7801–7806. <https://doi.org/10.1021/es800391s>
- Bowen, H. J. M. (1979). *Environmental chemistry of the elements*. Academic Press.
- Bowen, H. J. M. (1982). Boron, aluminum, gallium, indium, thallium. In *Environmental chemistry*, 2 (pp. 159–161). Royal Society of Chemistry.
- Brookins, D. G. (1988). *Eh-pH diagrams for geochemistry* (pp. 46–49). Springer Science & Business Media. [https://doi.org/10.1007/978-3-642-73093-1\\_18](https://doi.org/10.1007/978-3-642-73093-1_18)
- Brown, H., & Goldberg, E. (1949). The neutron pile as a tool in quantitative analysis; the gallium and palladium content of iron meteorites. *Science*, 109(2832), 347–353. <https://doi.org/10.1126/science.109.2832.347>

- Brown, M. T., Lippiatt, S. M., & Bruland, K. W. (2010). Dissolved aluminum, particulate aluminum, and silicic acid in northern Gulf of Alaska coastal waters: Glacial/riverine inputs and extreme reactivity. *Marine Chemistry*, 122(1), 160–175. <https://doi.org/10.1016/j.marchem.2010.04.002>
- Bruland, K. (1983). Trace elements in seawater. In J. P. Riley, & R. Chester (Eds.), *Chemical oceanography* (2nd ed., Vol. 8, pp. 147–220). Academic. <https://doi.org/10.1016/b978-0-12-588608-6.50009-2>
- Bruland, K., & Lohan, M. (2003). Controls of trace metals in seawater. In H. D. Holland, & K. K. Turekian (Eds.), *Treatise on geochemistry* (pp. 23–47). Pergamon. <https://doi.org/10.1016/b0-08-043751-6/06105-3>
- Burke, J., Handy, R. D., & Roast, S. D. (2003). Effect of low salinity on cadmium accumulation and calcium homeostasis in the shore crab (*Carcinus maenas*) at fixed free Cd<sup>2+</sup> concentrations. *Environmental Toxicology & Chemistry*, 22(11), 2761–2767. <https://doi.org/10.1897/02-410>
- Burton, J. D., Culkin, F., & Riley, J. P. (1959). The abundances of gallium and germanium in terrestrial materials. *Geochimica et Cosmochimica Acta*, 16(1–3), 151–180. [https://doi.org/10.1016/0016-7037\(59\)90052-3](https://doi.org/10.1016/0016-7037(59)90052-3)
- Butler, J. R. (1953). The geochemistry and mineralogy of rock weathering (1) the Lizard area, Cornwall. *Geochimica et Cosmochimica Acta*, 4, 157–178. [https://doi.org/10.1016/0016-7037\(53\)90013-1](https://doi.org/10.1016/0016-7037(53)90013-1)
- Butler, J. R. (1954). The geochemistry and mineralogy of rock weathering. (2) The Nordmarka area, Oslo. *Geochimica et Cosmochimica Acta*, 6(5–6), 268–281. [https://doi.org/10.1016/0016-7037\(54\)90005-8](https://doi.org/10.1016/0016-7037(54)90005-8)
- Campbell, A. J., & Humayun, M. (2005). Compositions of group IVB iron meteorites and their parent melt. *Geochimica et Cosmochimica Acta*, 69(19), 4733–4744. <https://doi.org/10.1016/j.gca.2005.06.004>
- Chen, Z. Y., Chen, Z. L., & Zhang, W. G. (1997). Quaternary stratigraphy and trace-element indices of the Yangtze Delta, Eastern China, with special reference to marine transgressions. *Quaternary Research*, 47(2), 181–191. <https://doi.org/10.1006/qres.1996.1878>
- Chen-Lin, C., Baedeker, P. A., & Wasson, J. T. (1976). Allende inclusions: Volatile-element distribution and evidence for incomplete volatilization of presolar solids. *Geochimica et Cosmochimica Acta*, 40(1), 85–94. [https://doi.org/10.1016/0016-7037\(76\)90196-4](https://doi.org/10.1016/0016-7037(76)90196-4)
- Choi, B.-G., Ouyang, X., & Wasson, J. T. (1995). Classification and origin of IAB and IIICD iron meteorites. *Geochimica et Cosmochimica Acta*, 59(3), 593–612. [https://doi.org/10.1016/0016-7037\(94\)00384-x](https://doi.org/10.1016/0016-7037(94)00384-x)
- Chou, L., & Wollast, R. (1997). Biogeochemical behavior and mass balance of dissolved aluminum in the western Mediterranean Sea. *Deep Sea Research Part II: Topical Studies in Oceanography*, 44(3–4), 741–768. [https://doi.org/10.1016/s0967-0645\(96\)00092-6](https://doi.org/10.1016/s0967-0645(96)00092-6)
- Clarke, E. T., & Martell, A. E. (1992). 1-Methyl-3-hydroxy-2-pyridinone and 1,4-dihydroxy-2-pyridinone complexes of the trivalent metal ions of iron(III), gallium(III), aluminum(III), indium(III) and gadolinium(III): Potentiometric and spectrophotometric determination of stabilities. *Inorganica Chimica Acta*, 196(2), 185–194. [https://doi.org/10.1016/s0020-1693\(00\)86122-8](https://doi.org/10.1016/s0020-1693(00)86122-8)
- Cobb, J. C. (1967). A trace-element study of iron meteorites. *Journal of Geophysical Research*, 72. <https://doi.org/10.1029/jz072i004p01329>
- Cobb, J. C., & Moran, G. (1965). Gallium concentrations in the metal phases of various meteorites. *Journal of Geophysical Research*, 70(20), 5309–5311. <https://doi.org/10.1029/jz070i020p05309>
- Colombo, M., Brown, K. A., De Vera, J., Bergquist, B. A., & Orians, K. J. (2019). Trace metal geochemistry of remote rivers in the Canadian Arctic Archipelago. *Chemical Geology*, 525, 479–491. <https://doi.org/10.1016/j.chemgeo.2019.08.006>
- Connelly, J. N., Bizzarro, M., Krot, A. N., Nordlund, Å., Wielandt, D., & Ivanova, M. A. (2012). The absolute chronology and thermal processing of solids in the solar protoplanetary disk. *Science*, 338(6107), 651–655. <https://doi.org/10.1126/science.1226919>
- Cornec, E. (1919). *Etude spectrographique des cendres de plantes marines* (Vol. 168, pp. 513–514). CR Acad. Sci.
- Creech, J. B., & Moynier, F. (2019). Tin and zinc stable isotope characterisation of chondrites and implications for early Solar System evolution. *Chemical Geology*, 511, 81–90. <https://doi.org/10.1016/j.chemgeo.2019.02.028>
- Culkin, F., & Riley, J. P. (1958a). The occurrence of gallium in marine organisms. *Journal of the Marine Biological Association of the United Kingdom*, 37(3), 607–615. <https://doi.org/10.1017/s0025315400005658>
- Culkin, F., & Riley, J. P. (1958b). The spectrophotometric determination of gallium in rocks and minerals. *Analyst*, 83(985), 11160–11166. <https://doi.org/10.1039/an9588300208>
- Daly, R. A. (1933). *Igneous rocks and the depths of the Earth*.
- Davis, A. M. (2006). Volatile evolution and loss. In *Meteorites and the early solar system II* (pp. 295–307). <https://doi.org/10.2307/j.ctv1v7zdm.20>
- Davis, F. A., Humayun, M., Hirschmann, M. M., & Cooper, R. S. (2013). Experimentally determined mineral/melt partitioning of first-row transition elements (FRTE) during partial melting of peridotite at 3 GPa. *Geochimica et Cosmochimica Acta*, 104, 232–260. <https://doi.org/10.1016/j.gca.2012.11.009>
- De Argollo, R., & Schilling, J.-G. (1978). Ge-Si and Ga-Al fractionation in Hawaiian volcanic rocks. *Geochimica et Cosmochimica Acta*, 42(6), 623–630. [https://doi.org/10.1016/0016-7037\(78\)90007-8](https://doi.org/10.1016/0016-7037(78)90007-8)
- Del Campo, A., & Rodeja, V. (1914). Espectrografia oceanografica. *Anales de la Real Sociedad Española de Química*, 12, 78.
- Dellinger, M., Gaillardet, J., Bouchez, J., Calmels, D., Galy, V., Hilton, R. G., et al. (2014). Lithium isotopes in large rivers reveal the cannibalistic nature of modern continental weathering and erosion. *Earth and Planetary Science Letters*, 401(4), 359–372. <https://doi.org/10.1016/j.epsl.2014.05.061>
- Dembiński, W., Herdzik, I., Skwara, W., Bulska, E., & Wysocka, A. (2006). Isotope effects of gallium and indium in cation exchange chromatography. *Nukleonika*, 51(4), 217–220.
- Diakonov, I. I. (1995). *Etude expérimentale de la complexation de l'aluminium avec l'ion sodium et de la spéciation du gallium et du fer (III) dans les solutions naturelles* (Unpublished PhD Thesis, p. 166). Paul-Sabatier University Toulouse.
- Diakonov, I. I., Pokrovski, G. S., Bénéthet, P., Schott, J., Dandurand, J. L., & Escalier, J. (1997). Gallium speciation in aqueous solution. Experimental study and modelling: Part 1. Thermodynamic properties of Ga(OH)<sup>4-</sup> to 300°C. *Geochimica et Cosmochimica Acta*, 61(7), 1333–1343. [https://doi.org/10.1016/s0016-7037\(97\)00011-2](https://doi.org/10.1016/s0016-7037(97)00011-2)
- Dupré, B., Viers, J., Dandurand, J.-L., Polve, M., Bénéthet, P., Vervier, P., & Braun, J.-J. (1999). Major and trace elements associated with colloids in organic-rich river waters: Ultrafiltration of natural and spiked solutions. *Chemical Geology*, 160(1–2), 63–80. [https://doi.org/10.1016/s0009-2541\(99\)00060-1](https://doi.org/10.1016/s0009-2541(99)00060-1)
- Dupuis, R. D. (1984). Metalorganic chemical vapor deposition of III-V semiconductors. *Science*, 226(4675), 623–629. <https://doi.org/10.1126/science.226.4675.623>
- Dvornikov, A., Ovsyannikova, L., & Sidenko, O. (1976). Some peculiarities of biological absorption-coefficients and of biogeochemical coefficients in hydrothermal deposits of Donbas in connection with prognostication of hidden mercury mineralization. *Geokhimiya*, 4, 626–633.
- El Korh, A., Luais, B., Boiron, M.-C., Deloule, E., & Cividini, D. (2017). Investigation of Ge and Ga exchange behaviour and Ge isotopic fractionation during subduction zone metamorphism. *Chemical Geology*, 449, 165–181. <https://doi.org/10.1016/j.chemgeo.2016.11.017>

- Emery, T., & Hoffer, P. B. (1980). Siderophore-mediated mechanism of gallium uptake demonstrated in the microorganism *Ustilago sphaerogena*. *Journal of Nuclear Medicine Official Publication Society of Nuclear Medicine*, 21(10), 935–939.
- Evans, B. W. (1964). Fractionation of elements in the pelitic hornfelses of the Cashel-Lough Wheelau intrusion. *Geochimica et Cosmochimica Acta*, 28(2), 127–156. [https://doi.org/10.1016/0016-7037\(64\)90146-2](https://doi.org/10.1016/0016-7037(64)90146-2)
- Evans, K. (2012). The redox budget of subduction zones. *Earth-Science Reviews*, 113(1–2), 11–32. <https://doi.org/10.1016/j.earscirev.2012.03.003>
- Feng, L. I., Zhou, L., Liu, J., & Hu, Z. (2019). Determination of gallium isotopic compositions in reference materials. *Geostandards and Geoanalytical Research*, 43(4). <https://doi.org/10.1111/ggr.12294>
- Fleischer, M. (1955). Estimates of the abundances of some chemical elements and their reliability. *Gaceta Sanitaria*, 27(5), 450–453.
- Fouché, K. F., & Smales, A. A. (1967). The distribution of trace elements in chondritic meteorites. 1. Gallium, germanium and indium. *Chemical Geology*, 2, 33. [https://doi.org/10.1016/0009-2541\(67\)90002-2](https://doi.org/10.1016/0009-2541(67)90002-2)
- French, S. J., Saunders, D. J., & Ingle, G. W. (1938). The system gallium-indium. *The Journal of Physical Chemistry*, 42(2), 265–274. <https://doi.org/10.1021/j100897a011>
- Frenzel, M., Hirsch, T., & Gutzmer, J. (2016). Gallium, germanium, indium, and other trace and minor elements in sphalerite as a function of deposit type—A meta-analysis. *Ore Geology Reviews*, 76, 52–78. <https://doi.org/10.1016/j.oregeorev.2015.12.017>
- Fryklund, V. C., & Fletcher, J. D. (1956). Geochemistry of sphalerite from the Star Mine, Coeur d'Alene district, Idaho. *Economic Geology*, 51, 223–247. <https://doi.org/10.2113/gsecongeo.51.3.223>
- Gaillardet, J., Viers, J., & Dupré, B. (2003). Trace elements in river waters. *Treatise on Geochemistry*, 5(Suppl 1), 195–235. <https://doi.org/10.1016/b0-08-043751-6/05165-3>
- Gaillardet, J., Viers, J., & Dupré, B. (2004). Trace elements in river waters. In *Treatise on geochemistry: Surface and ground water, weathering, and soils*. Elsevier.
- Gaillardet, J., Viers, J., & Dupré, B. (2014). Trace elements in river waters. In H. D. Holland, & K. K. Turekian (Eds.), *Treatise on geochemistry* (pp. 195–235). <https://doi.org/10.1016/b978-0-08-095975-7.00507-6>
- Gale, A., Dalton, C. A., Langmuir, C. H., Su, Y., & Schilling, J. G. (2013). The mean composition of ocean ridge basalts. *Geochemistry, Geophysics, Geosystems*, 14(3), 489–518. <https://doi.org/10.1029/2012gc004334>
- Gascoyne, D. J., Connor, J. A., & Bull, A. T. (1991). Capacity of siderophore—Producing alkalophilic bacteria to accumulate iron, gallium and aluminum. *Applied Microbiology and Biotechnology*, 36(1), 136–141. <https://doi.org/10.1007/bf00164714>
- German, C. R., & Seyfried, W. E., Jr. (2014). 8.7—Hydrothermal processes. In H. D. Holland, & K. L. Turekian (Eds.), *Treatise on geochemistry* (2nd ed., pp. 191–233). Elsevier. <https://doi.org/10.1016/b978-0-08-095975-7.00607-0>
- Goguel, R. (1988). Ultratrace metal analysis of New Zealand geothermal waters by ICP-MS. In *Proceedings New Zealand Trace Elements Group Conference Lincoln College* (pp. 263–270).
- Goldberg, E., Uchiyama, A., & Brown, H. (1951). The distribution of nickel, cobalt, gallium, palladium and gold in iron meteorites. *Geochimica et Cosmochimica Acta*, 2(1), 1–25. [https://doi.org/10.1016/0016-7037\(57\)90088-1](https://doi.org/10.1016/0016-7037(57)90088-1)
- Goldberg, E. D., & Arrhenius, G. (1958). Chemistry of Pacific pelagic sediments. *Geochimica et Cosmochimica Acta*, 13(2–3), 153–212. [https://doi.org/10.1016/0016-7037\(58\)90046-2](https://doi.org/10.1016/0016-7037(58)90046-2)
- Goldberg, L., Muller, E. A., & Aller, L. H. (1960). The abundances of the elements in the solar atmosphere. *The Astrophysical Journal - Supplement Series*, 45, 1. <https://doi.org/10.1086/190053>
- Goldschmidt, V. M. (1954). Geochemistry. *Soil Science*, 78(2), 156. <https://doi.org/10.1097/00010694-195408000-00019>
- Goldschmidt, V. M., & Peters, C. (1933). *Zur Geochemie des Germaniums*.
- Goodyear, J., & Steigmann, G. A. (1963). The crystal structure of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub>. *Acta Crystallographica*, 16. <https://doi.org/10.1107/s0365110x63002565>
- Gorham, E., & Swaine, D. (1965). The influence of oxidizing and reducing conditions upon the distribution of some elements in lake sediments. *Limnology & Oceanography*, 10(2), 268–279. <https://doi.org/10.4319/lo.1965.10.2.0268>
- Goss, C. H., Kaneko, Y., Khuu, L., Anderson, G. D., Ravishankar, S., Aitken, M. L., et al. (2018). Gallium disrupts bacterial iron metabolism and has therapeutic effects in mice and humans with lung infections. *Science Translational Medicine*, 10(460), 7520. <https://doi.org/10.1126/scitranslmed.aat7520>
- Greenland, L. (1965). Gallium in chondritic meteorites. *Journal of Geophysical Research*, 70(16), 3813–3817. <https://doi.org/10.1029/jz070i016p03813>
- Grevesse, N., & Sauval, A. J. (2002). The composition of the solar photosphere. *Advances in Space Research*, 30(1), 3–11. [https://doi.org/10.1016/s0273-1177\(02\)00170-9](https://doi.org/10.1016/s0273-1177(02)00170-9)
- Gribovskaya, I., Letunova, S., & Romanova, S. (1968). Microelements in the organs of legume plants. *Agrokhimiya*, 3, 81.
- Gross, J., & Thoennessen, M. (2012). Discovery of gallium, germanium, lutetium, and hafnium isotopes. *Atomic Data and Nuclear Data Tables*, 98(5), 983–1002. <https://doi.org/10.1016/j.adt.2011.09.004>
- Grossman, L., Ebel, D. S., & Simon, S. B. (2002). Formation of refractory inclusions by evaporation of condensate precursors. *Geochimica et Cosmochimica Acta*, 66(1), 145–161. [https://doi.org/10.1016/s0016-7037\(01\)00731-1](https://doi.org/10.1016/s0016-7037(01)00731-1)
- Gussone, N., Schmitt, A. D., Heuser, A., Wombacher, F., Dietzel, M., Tipper, E., & Schiller, M. (2016). *Advances in isotope geochemistry*.
- Hall, L. W., & Anderson, R. D. (1995). The influence of salinity on the toxicity of various classes of chemicals to aquatic biota. *Critical Reviews in Toxicology*, 25(4), 281–346. <https://doi.org/10.3109/10408449509021613>
- Hecht, F., & Fenninger, H. (1965). Determination of trace elements in meteorites. *Progress in Oceanography*, 3, 145–148. [https://doi.org/10.1016/0079-6611\(65\)90013-3](https://doi.org/10.1016/0079-6611(65)90013-3)
- Hewitt, E., & Bolle-Jones, E. W. (1952). Investigations on possible micronutrient elements for higher plants. I. Experiments with cobalt, nickel and gallium in sand culture. In *Annual report long Ashton agricultural horticultural research station*.
- Hieronimus, B., Boulegue, J., & Kotschoubey, B. (1990). Gallium behaviour in some intertropical environment alterations. *Chemical Geology*, 84(1–4), 78–82. [https://doi.org/10.1016/0009-2541\(90\)90169-8](https://doi.org/10.1016/0009-2541(90)90169-8)
- Hieronimus, B., Kotschoubey, B., & Boulègue, J. (2001). Gallium behaviour in some contrasting lateritic profiles from Cameroon and Brazil. *Journal of Geochemical Exploration*, 72, 147–163. [https://doi.org/10.1016/s0375-6742\(01\)00160-1](https://doi.org/10.1016/s0375-6742(01)00160-1)
- Higazy, R. A. (1952). Behaviour of the trace elements in a front of metasomatic-metamorphism in the Dalradian of Co. Donegal. *Geochimica et Cosmochimica Acta*, 2(3), 170–184. [https://doi.org/10.1016/0016-7037\(52\)90005-7](https://doi.org/10.1016/0016-7037(52)90005-7)
- Hindshaw, R. S., Reynolds, B. C., Wiederhold, J. G., Kretzschmar, R., & Bourdon, B. (2011). Calcium isotopes in a proglacial weathering environment: Damma glacier, Switzerland. *Geochimica et Cosmochimica Acta*, 75(1), 106–118. <https://doi.org/10.1016/j.gca.2010.09.038>
- Ho, P., Resing, J. A., & Shiller, A. M. (2019). Processes controlling the distribution of dissolved Al and Ga along the U.S. geotraces East Pacific zonal transect (gp16). *Deep Sea Research Part I: Oceanographic Research Papers*, 147, 128–145. <https://doi.org/10.1016/j.dsr.2019.04.009>



- Hose, H. R. (2016). Bauxite mineralogy. In D. Donaldson, & B. E. Raahauge (Eds.), *Essential readings in light metals* (pp. 21–29). [https://doi.org/10.1007/978-3-319-48176-0\\_2](https://doi.org/10.1007/978-3-319-48176-0_2)
- Hu, Z., & Gao, S. (2008). Upper crustal abundances of trace elements: A revision and update. *Chemical Geology*, 253(3–4), 205–221. <https://doi.org/10.1016/j.chemgeo.2008.05.010>
- Huang, Y., Shen, H., Chen, H., Wang, R., Zhang, Y., Su, S., et al. (2014). Quantification of global primary emissions of PM<sub>2.5</sub>, PM<sub>10</sub>, and TSP from combustion and industrial process sources. *Environmental Science & Technology*, 48(23), 13834–13843. <https://doi.org/10.1021/es503696k>
- Hunt, J. M. (1972). Distribution of carbon in crust of earth. *AAPG Bulletin*, 56(11), 2273–2277. <https://doi.org/10.1306/819a4206-16c5-11d7-8645000102c1865d>
- Hutchinson, G. E., & Wollack, A. (1943). *Biological accumulators of aluminum*. Connecticut Academy of Arts and Sciences.
- Hydes, D. J. (1979). Aluminum in seawater: Control by inorganic processes. *Science*, 205(4412), 1260–1262. <https://doi.org/10.1126/science.205.4412.1260>
- Hydes, D. J. (1983). Distribution of aluminium in waters of the North East Atlantic 25°N to 35°N. *Geochimica et Cosmochimica Acta*, 47(5), 967–973. [https://doi.org/10.1016/0016-7037\(83\)90164-3](https://doi.org/10.1016/0016-7037(83)90164-3)
- Hydes, D. J., & Liss, P. S. (1977). The behaviour of dissolved aluminium in estuarine and coastal waters. *Estuarine and Coastal Marine Science*, 5(6), 755–769. [https://doi.org/10.1016/0302-3524\(77\)90047-0](https://doi.org/10.1016/0302-3524(77)90047-0)
- Inghram, M. G., Hess, D. C., Brown, H. S., & Goldberg, E. (1948). On the isotopic composition of meteoritic and terrestrial gallium. *Physical Review*, 74(3), 343–344. <https://doi.org/10.1103/physrev.74.343.2>
- Ishiguro, T., Koga, N., & Matsuo, Y. (1952). Studies on the constituents of ambergris. 2. Inorganic constituents of ambergris. *Yakugaku Zasshi-Journal of the pharmaceutical society of Japan*, 72(11), 1439–1443. [https://doi.org/10.1248/yakushi1947.72.11\\_1439](https://doi.org/10.1248/yakushi1947.72.11_1439)
- Johnson, K. (2016). *Periodic table of elements in the ocean*.
- Kabata-Pendias, A. (2010). *Trace elements in soils and plants* (4th ed.). Crc Press.
- Kato, C., & Moynier, F. (2017a). Gallium isotopic evidence for the fate of moderately volatile elements in planetary bodies and refractory inclusions. *Earth and Planetary Science Letters*, 479, 330–339. <https://doi.org/10.1016/j.epsl.2017.09.028>
- Kato, C., & Moynier, F. (2017b). Gallium isotopic evidence for extensive volatile loss from the Moon during its formation. *Science Advances*, 3(7), e1700571. <https://doi.org/10.1126/sciadv.1700571>
- Kato, C., Moynier, F., Foriel, J., Teng, F. Z., & Puchtel, I. S. (2017). The gallium isotopic composition of the bulk silicate Earth. *Chemical Geology*, 448, 164–172. <https://doi.org/10.1016/j.chemgeo.2016.11.020>
- Katrak, F. E., & Agarwal, J. C. (1981). Gallium: Long-run supply. *Journal of Metals*, 33(9), 33–36. <https://doi.org/10.1007/bf03339492>
- King, R. B., Lawrence, G. M., & Link, J. K. (1965). Solar abundances of gallium, silver, and indium. *The Astrophysical Journal*, 142, 386. <https://doi.org/10.1086/148295>
- Kiriya, T., & Kuroda, R. (1988). Anion-exchange enrichment and spectrophotometric determination of traces of gallium in natural waters. *Fresenius' Zeitschrift für Analytische Chemie*, 332(4), 338–340. <https://doi.org/10.1007/bf00468811>
- Koljonen, T. E. (1992). *The geochemical atlas of Finland, Part 2. Till* (p. 218). Geological Survey of Finland.
- Kramer, J., Laan, P., Sarthou, G., Timmermans, K. R., & Baar, H. J. W. D. (2004). Distribution of dissolved aluminium in the high atmospheric input region of the subtropical waters of the North Atlantic Ocean. *Marine Chemistry*, 88(3), 85–101. <https://doi.org/10.1016/j.marchem.2004.03.009>
- Krupp, R. E., & Seward, T. M. (1990). Transport and deposition of metals in the Rotokawa geothermal system, New Zealand. *Mineralium Deposita*, 25(1), 73–81. <https://doi.org/10.1007/bf03326387>
- Laeter, J. R. D. (1972). The isotopic composition and elemental abundance of gallium in meteorites and in terrestrial samples. *Geochimica et Cosmochimica Acta*, 36(7), 735–743. [https://doi.org/10.1016/0016-7037\(72\)90084-1](https://doi.org/10.1016/0016-7037(72)90084-1)
- Le Roux, V., Dasgupta, R., & Lee, C.-T. A. (2015). Recommended mineral-melt partition coefficients for FRTEs (Cu), Ga, and Ge during mantle melting. *American Mineralogist*, 100, 2533–2544. <https://doi.org/10.2138/am-2015-5215>
- Li, T. (1985). The abundance of chemical elements in the lithosphere and its structural layers. *Acta Geologica Sinica*, 3, 219–227. in Chinese.
- Lin, H. C., & Dunson, W. A. (1993). The effect of salinity on the acute toxicity of cadmium to the tropical, estuarine, hermaphroditic fish, *Rivulus marmoratus*: A comparison of Cd, Cu, and Zn tolerance with *Fundulus heteroclitus*. *Archives of Environmental Contamination and Toxicology*, 25(1), 41–47. <https://doi.org/10.1007/bf00230709>
- Liu, F., Yu, Y., Yi, L., & Liu, J. (2016). Liquid metal as reconnection agent for peripheral nerve injury. *Science Bulletin*, 61(12), 939–947. <https://doi.org/10.1007/s11434-016-1090-2>
- Liu, S., Wang, Z., Zhang, Y., Liu, Y., Yuan, W., Zhang, T., et al. (2019). Distribution and partitioning of heavy metals in large anthropogenically impacted river, the Pearl River, China. *Acta Geochimica*, 38(2), 216–231. <https://doi.org/10.1007/s11631-018-00309-7>
- Lodders, K. (2003). Solar system abundances and condensation temperatures of the elements. *The Astrophysical Journal*, 591(2), 1220–1247. <https://doi.org/10.1086/375492>
- Lodders, K., & Fegley, B. (1998). *The planetary scientist's companion*.
- Lodders, K., Palme, H., & Gail, H. P. (2009). Abundances of the elements in the solar system. In J. E. Trümper (Ed.), *Landolt-Börnstein, new series, astronomy and astrophysics* (pp. 560–630). Springer-Verlag.
- Lounamaa, J. (1956). *Trace elements in plants growing wild on different rocks in Finland: A semi-quantitative spectrographic survey: Selostus: Erilaisilla Kalliolla Suomessa Luonnonvaraisina Kasvneiden Kasvien Hivenaineista*, 29. Suomalaisen Kirjallisuuden Kirjapaino oy.
- Lovering, J. F., Nichiporuk, W., Chodos, A., & Brown, H. (1957). The distribution of gallium, germanium, cobalt, chromium, and copper in iron and stony-iron meteorites in relation to nickel content and structure. *Geochimica et Cosmochimica Acta*, 11(4), 263–278. [https://doi.org/10.1016/0016-7037\(57\)90099-6](https://doi.org/10.1016/0016-7037(57)90099-6)
- Løvik, A. N., Restrepo, E., & Müller, D. B. (2015). The global anthropogenic gallium system: Determinants of demand, supply and efficiency improvements. *Environmental Science & Technology*, 49(9), 5704–5712.
- Luck, J.-M., Othman, D. B., & Albarède, F. (2005). Zn and Cu isotopic variations in chondrites and iron meteorites: Early solar nebula reservoirs and parent-body processes. *Geochimica et Cosmochimica Acta*, 69(22), 5351–5363. <https://doi.org/10.1016/j.gca.2005.06.018>
- Macdonald, R., Rogers, N. W., Baginski, B., & Dzianowski, P. (2010). Distribution of gallium between phenocrysts and melt in peralkaline salic volcanic rocks, Kenya Rift Valley. *Mineralogical Magazine*, 74, 351–363. <https://doi.org/10.1180/minmag.2010.074.2.351>
- Machlan, L., Gramlich, J., Powell, L., & Lambert, G. (1986). Absolute isotopic abundance ratio and atomic weight of a reference sample of gallium. *Journal of Research of the National Bureau of Standards*, 91(6), 323–331. <https://doi.org/10.6028/jres.091.036>
- Machlan, L. A., & Gramlich, J. W. (1988). Isotopic fractionation of gallium on an ion-exchange column. *Analytical Chemistry*, 60(1), 37–39. <https://doi.org/10.1021/ac00152a011>

- Maghakyan, N., Tepanosyan, G., Belyaeva, O., Sahakyan, L., & Saghatelyan, A. (2017). Assessment of pollution levels and human health risk of heavy metals in dust deposited on Yerevan's tree leaves (Armenia). *Acta Geochimica*, 36(1), 16–26. <https://doi.org/10.1007/s11631-016-0122-6>
- Malvin, D. J., & Drake, M. J. (1987). Experimental determination of crystal/melt partitioning of Ga and Ge in the system forsterite-anorthite-diopside. *Geochimica et Cosmochimica Acta*, 51(8), 2117–2128. [https://doi.org/10.1016/0016-7037\(87\)90260-2](https://doi.org/10.1016/0016-7037(87)90260-2)
- Mann, U., Frost, D. J., & Rubie, D. C. (2009). Evidence for high-pressure core-mantle differentiation from the metal–silicate partitioning of lithophile and weakly-siderophile elements. *Geochimica et Cosmochimica Acta*, 73(24), 7360–7386. <https://doi.org/10.1016/j.gca.2009.08.006>
- Maréchal, C. N., Télouk, P., & Albarède, F. (1999). Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology*, 156(1–4), 251–273. [https://doi.org/10.1016/S0009-2541\(98\)00191-0](https://doi.org/10.1016/S0009-2541(98)00191-0)
- Maring, H., & Duce, R. (1987). The impact of atmospheric aerosols on trace metal chemistry in open ocean surface seawater, 1. Aluminum. *Earth and Planetary Science Letters*, 84(4), 381–392. [https://doi.org/10.1016/0012-821x\(87\)90003-3](https://doi.org/10.1016/0012-821x(87)90003-3)
- Matkovic, V., Apseloff, G., Shepard, D., & Gerber, N. (1990). Use of gallium to treat Paget's disease of bone: A pilot study. *The Lancet*, 335(8681), 72–75. [https://doi.org/10.1016/0140-6736\(90\)90540-1](https://doi.org/10.1016/0140-6736(90)90540-1)
- Matkovic, V., & Gerber, N. (1992). Method of treating arthritis using gallium compounds. *Google Patents*.
- Matschullat, J. (2000). Arsenic in the geosphere—A review. *The Science of the Total Environment*, 249(1–3), 297–312. [https://doi.org/10.1016/S0048-9697\(99\)00524-0](https://doi.org/10.1016/S0048-9697(99)00524-0)
- Mcalister, J., & Orians, K. (2012). Calculation of river-seawater endmembers and differential trace metal scavenging in the Columbia River plume. *Estuarine, Coastal and Shelf Science*, 99(99), 31–41. <https://doi.org/10.1016/j.ecss.2011.12.013>
- McDonough, W. F. (1990a). Comment on "abundance and distribution of gallium in some spinel and garnet lherzolites" by D. B. McKay and R. H. Mitchell. *Geochimica et Cosmochimica Acta*, 54(2), 471–473. [https://doi.org/10.1016/0016-7037\(90\)90335-i](https://doi.org/10.1016/0016-7037(90)90335-i)
- McDonough, W. F. (1990b). Constraints on the composition of the continental lithospheric mantle. *Earth and Planetary Science Letters*, 101(1), 1–18. [https://doi.org/10.1016/0012-821x\(90\)90119-i](https://doi.org/10.1016/0012-821x(90)90119-i)
- McDonough, W. F. (2003). Compositional model for the Earth's core. In R. W. Carlson (Ed.), *Treatise on geochemistry, the mantle and core* (Vol. 2, pp. 547–568). Elsevier Press. <https://doi.org/10.1016/b0-08-043751-6/02015-6>
- McDonough, W. F., & Sun, S. S. (1995). The composition of the Earth. *Chemical Geology*, 120(3–4), 223–253. [https://doi.org/10.1016/0009-2541\(94\)00140-4](https://doi.org/10.1016/0009-2541(94)00140-4)
- Measures, C. (1995). The distribution of Al in the IOC stations of the eastern Atlantic between 30°S and 34°N. *Marine Chemistry*, 49(4), 267–281. [https://doi.org/10.1016/0304-4203\(95\)00017-1](https://doi.org/10.1016/0304-4203(95)00017-1)
- Measures, C. I., & Edmond, J. M. (1988). Aluminium as a tracer of the deep outflow from the Mediterranean. *Journal of Geophysical Research*, 93(C1), 591–595. <https://doi.org/10.1029/jc093ic01p00591>
- Merryman, J. I., Capen, C. C., & Rosol, T. J. (1994). Effects of gallium nitrate in nude mice bearing a canine adenocarcinoma (CAC-8) model of humoral hypercalcemia of malignancy. *Journal of Bone and Mineral Research*, 9(5), 725–732.
- Metz, S., & Trefry, J. H. (2000). Chemical and mineralogical influences on concentrations of trace metals in hydrothermal fluids. *Geochimica et Cosmochimica Acta*, 64(13), 2267–2279. [https://doi.org/10.1016/S0016-7037\(00\)00354-9](https://doi.org/10.1016/S0016-7037(00)00354-9)
- Munir, H. (2018). Gallium. In W. M. White (Ed.), *Encyclopedia of geochemistry* (pp. 526–530). *Geochimica et Cosmochimica Acta*.
- Négre, P., Ladenberger, A., Reimann, C., Birke, M., & Sadeghi, M. (2018). Distribution of Rb, Ga and Cs in agricultural land soils at European continental scale (GEMAS): Implications for weathering conditions and provenance. *Chemical Geology*, 479, 188–203. <https://doi.org/10.1016/j.chemgeo.2018.01.009>
- Nesterenko, G., Studenikova, Z., & Savinova, E. J. G. (1958). *Rare and dispersed elements in skarns of Tyrny-Auz [Soviet Armenia]* (p. 287).
- Nielsen, S. G., Rehkämper, M., Teagle, D. A., Butterfield, D. A., Alt, J. C., & Halliday, A. N. (2006). Hydrothermal fluid fluxes calculated from the isotopic mass balance of thallium in the ocean crust. *Earth and Planetary Science Letters*, 251(1–2), 120–133. <https://doi.org/10.1016/j.epsl.2006.09.002>
- Niu, Y., Wilson, M., Humphreys, E. R., & O'Hara, M. J. (2012). A trace element perspective on the source of ocean island basalts (OIB) and fate of subducted ocean crust (SOC) and mantle lithosphere (SML). *Episodes*, 35(2), 310–327. <https://doi.org/10.18814/epiugs/2012/v35i2/002>
- Nockolds, S. R., & Mitchell, R. L. (1948). The geochemistry of some caledonian plutonic rocks: A study in the relationship between the major and trace elements of igneous rocks and their minerals. *Transactions of the Royal Society of Edinburgh*, 61(02), 533–575.
- Noddack, I. (1939). Die Häufigkeiten der Schwermetalle in Meerestieren. *Arkiv for Zoologi*, 32, 1–35.
- Nuamah, D. O. B., Tandoh, K. K., & Brako, A. B. (2019). Geochemistry of minor and trace elements in soils of Akuse Area, Southeastern Ghana. *Geosciences*, 9(1), 8–17.
- O'Neill, H. S. C., & Palme, H. (1998). Composition of the silicate Earth: Implications for accretion and core formation. In *The Earth's mantle, composition, structure and evolution* (pp. 3–126).
- Onikura, N., Nakamura, A., & Kishi, K. (2005). Acute toxicity of gallium and effects of salinity on gallium toxicity to brackish and marine organisms. *Bulletin of Environmental Contamination and Toxicology*, 75(2), 356–360. <https://doi.org/10.1007/s00128-005-0761-5>
- Onishi, H., & Sandell, E. B. (1956). Gallium in chondrites. *Geochimica et Cosmochimica Acta*, 9(1–2), 78–82. [https://doi.org/10.1016/0016-7037\(56\)90057-6](https://doi.org/10.1016/0016-7037(56)90057-6)
- Opfergelt, S., Georg, R. B., Delvaux, B., Cabidoche, Y. M., Burton, K. W., & Halliday, A. N. (2012). Mechanisms of magnesium isotope fractionation in volcanic soil weathering sequences, Guadeloupe. *Earth and Planetary Science Letters*, 341–344(8), 176–185. <https://doi.org/10.1016/j.epsl.2012.06.010>
- Orians, K. J., & Bruland, K. W. (1985). Dissolved aluminium in the central North Pacific. *Nature*, 316(6027), 427–429. <https://doi.org/10.1038/316427a0>
- Orians, K. J., & Bruland, K. W. (1986). The biogeochemistry of aluminium in the Pacific Ocean. *Earth and Planetary Science Letters*, 78(4), 397–410. [https://doi.org/10.1016/0012-821x\(86\)90006-3](https://doi.org/10.1016/0012-821x(86)90006-3)
- Orians, K. J., & Bruland, K. W. (1988a). Dissolved gallium in the open ocean. *Nature*, 332(6166), 717–719. <https://doi.org/10.1038/332717a0>
- Orians, K. J., & Bruland, K. W. (1988b). The marine geochemistry of dissolved gallium: A comparison with dissolved aluminum. *Geochimica et Cosmochimica Acta*, 52(12), 2955–2962. [https://doi.org/10.1016/0016-7037\(88\)90160-3](https://doi.org/10.1016/0016-7037(88)90160-3)
- Paniello, R. C., Day, J. M. D., & Moynier, F. (2012). Zinc isotopic evidence for the origin of the Moon. *Nature*, 490, 376–379. <https://doi.org/10.1038/nature11507>
- Paulson, A. J., & Balistrieri, L. (1999). Modeling removal of Cd, Cu, Pb, and Zn in acidic groundwater during neutralization by ambient surface waters and groundwaters. *Environmental Science & Technology*, 33(33), 3850–3856. <https://doi.org/10.1021/es9900454>
- Pearson, R. G. (1963). Hard and soft acids and bases. *Journal of the American Chemical Society*, 85(22). <https://doi.org/10.1021/ja00905a001>

- Pentlinghaus, H., & Bambauer, H. (1971). Substitution of Al (III), Ga (III), Fe (III), Si (IV) and Ge (IV) in synthetic alkali feldspars. *Neues Jahrbuch für Mineralogie - Monatshefte*, 416.
- Persson, P., Katarina Zivkovic, A., & Sjöberg, S. (2006). Quantitative adsorption and local structures of Gallium(III) at the water- $\alpha$ -FeOOH interface. *Langmuir*, 22(5), 2096–2104. <https://doi.org/10.1021/la052555j>
- Pokrovski, G. S., Schott, J., Farges, F., & Hazemann, J. L. (2003). Iron (III)-silica interaction in aqueous solution: Insights from X-ray-absorption fine structure spectroscopy. *Geochimica et Cosmochimica Acta*, 67, 3559–3573. [https://doi.org/10.1016/s0016-7037\(03\)00160-1](https://doi.org/10.1016/s0016-7037(03)00160-1)
- Pokrovski, G. S., Schott, J., Hazemann, J. L., Farges, F., & Pokrovsky, O. S. (2002). An X-ray absorption fine structure and nuclear magnetic resonance spectroscopy study of gallium-silica complexes in aqueous solution. *Geochimica et Cosmochimica Acta*, 66(24), 4203–4222. [https://doi.org/10.1016/s0016-7037\(02\)00973-0](https://doi.org/10.1016/s0016-7037(02)00973-0)
- Pokrovsky, O. S., Manasypov, R. M., Loiko, S. V., Krickov, I. A., & Kirpotin, S. N. (2015). Trace elements transport in western Siberia Rivers across a permafrost gradient. *Biogeosciences Discussions*, 12(21), 17857–17912. <https://doi.org/10.5194/bg-12-6301-2015>
- Pokrovsky, O. S., Pokrovski, G. S., & Schott, J. (2004). Gallium(III) adsorption on carbonates and oxides: X-ray absorption fine structure spectroscopy study and surface complexation modeling. *Journal of Colloid and Interface Science*, 279(2), 314–325. <https://doi.org/10.1016/j.jcis.2004.06.095>
- Pokrovsky, O. S., Pokrovski, G. S., & Schott, J. (2006). Experimental study of germanium adsorption on goethite and germanium coprecipitation with iron hydroxide: X-ray absorption fine structure and macroscopic characterization. *Geochimica et Cosmochimica Acta*, 70(13), 3325–3341. <https://doi.org/10.1016/j.gca.2006.04.012>
- Pokrovsky, O. S., & Schott, J. (2002a). Surface chemistry and dissolution kinetics of divalent metal carbonates. *Environmental Science & Technology*, 36(3), 426–432. <https://doi.org/10.1021/es010925u>
- Pokrovsky, O. S., & Schott, J. (2002b). Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chemical Geology*, 190, 141–179. [https://doi.org/10.1016/s0009-2541\(02\)00115-8](https://doi.org/10.1016/s0009-2541(02)00115-8)
- Pokrovsky, O. S., Schott, J., & Castillo, A. (2005). Kinetics of brucite dissolution at 25°C in the presence of organic and inorganic ligands and divalent metals. *Geochimica et Cosmochimica Acta*, 69(4), 905–918. <https://doi.org/10.1016/j.gca.2004.08.011>
- Pokrovsky, O. S., Viers, J., Shirokova, L. S., Shevchenko, V. P., Filipov, A. S., & Dupré, B. (2010). Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in the Severnaya Dvina River and its tributary. *Chemical Geology*, 273(1), 136–149. <https://doi.org/10.1016/j.chemgeo.2010.02.018>
- Polat, A., Appel, P. W. U., Fryer, B., Windley, B., Frei, R., Samson, I. M., & Huang, H. (2009). Trace element systematics of the Neoproterozoic Fiskensset anorthosite complex and associated meta-volcanic rocks, SW Greenland: Evidence for a magmatic arc origin. *Precambrian Research*, 175(1–4), 87–115. <https://doi.org/10.1016/j.precamres.2009.09.002>
- Poledniok, J. (2008). Speciation of scandium and gallium in soil. *Chemosphere*, 73(4), 572.
- Prince, A. L. (1957a). Influence of soil types on the mineral composition of corn tissues as determined spectrographically. *Soil Science*, 83(5), 399–406. <https://doi.org/10.1097/00010694-195705000-00007>
- Prince, A. L. (1957b). Trace element delivering capacity of 10 New Jersey soil types as measured by spectrographic analyses of soils and mature corn leaves. *Soil Science*, 84(5), 413–418. <https://doi.org/10.1097/00010694-195711000-00007>
- Pringle, E. A., & Moynier, F. (2017). Rubidium isotopic composition of the Earth, meteorites, and the Moon: Evidence for the origin of volatile loss during planetary accretion. *Earth and Planetary Science Letters*, 473, 62–70. <https://doi.org/10.1016/j.epsl.2017.05.033>
- Pringle, E. A., Moynier, F., Beck, P., Paniello, R., & Hezel, D. C. (2017). The origin of volatile element depletion in early solar system material: Clues from Zn isotopes in chondrules. *Earth and Planetary Science Letters*, 468, 62–71. <https://doi.org/10.1016/j.epsl.2017.04.002>
- Program, N. T. (2000). NTP toxicology and carcinogenesis studies of gallium arsenide (CAS No. 1303-00-0) in F344/N rats and B6C3F1 Mice (Inhalation Studies). *National Toxicology Program Technical Report Series*, 492, 1–306.
- Prokof'ev, V. Y., Naumov, V. B., & Dorofeeva, V. A. (2016). Gallium concentration in natural melts and fluids. *Geochemistry International*, 54(8), 691–705.
- Prospero, J. (1981). Eolian transport to the world ocean. *Sea*, 7, 801–874.
- Qin, S., Sun, Y., Li, Y., Wang, J., Zhao, C., & Gao, K. (2015). Coal deposits as promising alternative sources for gallium. *Earth-Science Reviews*, 150, 95–101. <https://doi.org/10.1016/j.earscirev.2015.07.010>
- Rankama, K. (1946). *On the geochemical differentiation in the earth's crust*. Government Press.
- Razenkova, N. I., & Galaktionova, G. F. (1962). On the mode of occurrence of gallium in the oxidized zone of sulfide deposits. In *Geochemistry (USSR) (English transl.)* (p. 104).
- Richardson, J. B., & Derry, L. A. (2016). Using gallium as a tracer of aluminum in the Critical Zone: Influences on terrestrial cycling from vegetation. In *AGU fall meeting abstracts*. AgU Fall Meeting.
- Riley, G. (1943). The toxicity of heavy metals to fouling organisms. In *Paper 12, sixth report from Woods Hole Oceanographic Institution to the Bureau of ships*.
- Riley, J. P. (2010). Composition of mineral water from the hot spring at bath. *Journal of Chemical Technology and Biotechnology*, 11(5), 190–192.
- Robinson, A. L. (1983). GaAs readied for high-speed microcircuits. *Science*, 219(4582), 275–277. <https://doi.org/10.1126/science.219.4582.275>
- Rosner, M. H., & Carter, D. E. (1987). Metabolism and excretion of gallium arsenide and arsenic oxides by hamsters following intratracheal instillation. *Fundamental and Applied Toxicology*, 9(4), 730–737. [https://doi.org/10.1016/0272-0590\(87\)90180-1](https://doi.org/10.1016/0272-0590(87)90180-1)
- Rudnick, R. L., & Fountain, D. M. (1995). Nature and composition of the continental crust: A lower crustal perspective. *Reviews of Geophysics*, 33(3), 267–309. <https://doi.org/10.1029/95rg01302>
- Rudnick, R. L., & Gao, S. (2003). Composition of the continental crust. *Treatise on Geochemistry*, 3, 659. <https://doi.org/10.1016/b0-08-043751-6/03016-4>
- Sandell, E. B. (1949). The gallium content of igneous rocks. *American Journal of Science*, 247(1), 40–48. <https://doi.org/10.2475/ajs.247.1.40>
- Savov, I. P., Ryan, J. G., D'Antonio, M., & Fryer, P. (2007). Shallow slab fluid release across and along the Mariana arc-basin system: Insights from geochemistry of serpentinized peridotites from the Mariana fore arc. *Journal of Geophysical Research*, B112. <https://doi.org/10.1029/2006JB004749>
- Schaudy, R., Kiesl, W., & Hecht, F. (1967). Activation analytical determination of elements in meteorites, 2: Determination of manganese, sodium, gallium, copper, gold and chromium in 21 meteorites. *Chemical Geology*, 3(4), 312.
- Schier, K., Ernst, D. M., Sousa, I. M. C., Garbe-Schönberg, D., Kuhn, T., Hein, J. R., & Bau, M. (2021). Gallium-aluminum systematics of marine hydrogenetic ferromanganese crusts: Inter-oceanic differences and fractionation during scavenging. *Geochimica et Cosmochimica Acta*. <https://doi.org/10.1016/j.gca.2021.05.019>
- Schulte, R. F., & Foley, N. K. (2013). *Compilation of gallium resource data for bauxite deposits* (pp. 2013–1272). U.S. Geological survey. Retrieved from <http://pubs.usgs.gov/of/2013/1272/pdf/ofr2013-1272.pdf>

- Shacklette, H., Erdman, J., Harms, T. F., & Papp, C. (1978). Trace elements in plant foodstuffs. In *Toxicity of heavy metals in the environment. Part 1* (pp. 25–68).
- Shacklette, H. T. (1965). *Element content of bryophytes*. US Govt. Print. Off.
- Shafer, J. T., Neal, C. R., & Castillo, P. R. (2004). Compositional variability in lavas from the Ontong Java Plateau: Results from basalt clasts within the volcanoclastic succession at Ocean Drilling Program Site 1184. *Geological Society London Special Publications*, 229(1), 333–351. <https://doi.org/10.1144/gsl.sp.2004.229.01.19>
- Shaw, D. M. (1957). The geochemistry of gallium, indium, thallium—A review. *Physics and Chemistry of the Earth*, 2, 164–211. [https://doi.org/10.1016/0079-1946\(57\)90009-5](https://doi.org/10.1016/0079-1946(57)90009-5)
- Shiller, A., Bairamadgi, G., Heidingsfelder, P., & Gross, L. (2006). Dissolved trace elements in surface waters of the Northwest Pacific Ocean. *EOS, Transactions, American Geophysical Union*, 87(36). <https://doi.org/10.1029/eost2006e08>
- Shiller, A. M. (1988). Enrichment of dissolved gallium relative to aluminum in natural waters. *Geochimica et Cosmochimica Acta*, 52(7), 1879–1882. [https://doi.org/10.1016/0016-7037\(88\)90011-7](https://doi.org/10.1016/0016-7037(88)90011-7)
- Shiller, A. M. (1998). Dissolved gallium in the Atlantic Ocean. *Marine Chemistry*, 61, 87–99. [https://doi.org/10.1016/s0304-4203\(98\)00009-7](https://doi.org/10.1016/s0304-4203(98)00009-7)
- Shiller, A. M., & Bairamadgi, G. R. (2006). Dissolved gallium in the northwest Pacific and the south and central Atlantic Oceans: Implications for aeolian Fe input and a reconsideration of profiles. *Geochemistry, Geophysics, Geosystems*, 7(8). <https://doi.org/10.1029/2005gc001118>
- Shiller, A. M., & Frilot, D. M. (1996). The geochemistry of gallium relative to aluminum in Californian streams. *Geochimica et Cosmochimica Acta*, 60(8), 1323–1328. [https://doi.org/10.1016/0016-7037\(96\)00002-6](https://doi.org/10.1016/0016-7037(96)00002-6)
- Siebert, J., Corgne, A., & Ryerson, F. J. (2011). Systematics of metal-silicate partitioning for many siderophile elements applied to Earth's core formation. *Geochimica et Cosmochimica Acta*, 75(6), 1451–1489. <https://doi.org/10.1016/j.gca.2010.12.013>
- Sitnin, A. A. (1960). *Distribution of rare elements in amazonite granites of the Etyka massif, eastern Transbaikalia*. (p. 361). Geochemistry (USSR) (English Transl.).
- Steinberg, R. A. (1938). The essentiality of gallium to growth and reproduction of *Aspergillus Niger*. *Journal of Agricultural Research*, 57, 569–574.
- Steinberg, R. A. (1939a). Effects of nitrogen compounds and trace elements on growth of *Aspergillus Niger*. *Journal of Agricultural Research*, 59, 731–748.
- Steinberg, R. A. (1939b). Relation of carbon nutrition to trace-element and accessory requirements of *Aspergillus Niger*. *Journal of Agricultural Research*, 59, 749–763.
- Steinberg, R. A. (1941). Use of Lemna for nutrition studies on green plants. *Journal of Agricultural Research*, 62, 423–430.
- Stoffyn, M., & Mackenzie, F. T. (1982). Fate of dissolved aluminum in the oceans. *Marine Chemistry*, 11(2), 105–127. [https://doi.org/10.1016/0304-4203\(82\)90036-6](https://doi.org/10.1016/0304-4203(82)90036-6)
- Stoffyn-Egli, P. (1982). Dissolved aluminium in interstitial waters of recent terrigenous marine sediments from the North Atlantic Ocean. *Geochimica et Cosmochimica Acta*, 46(8), 1345–1352. [https://doi.org/10.1016/0016-7037\(82\)90270-8](https://doi.org/10.1016/0016-7037(82)90270-8)
- Strunz, H. (1965). Söhngkeit, Ga(OH)<sub>3</sub>, ein neues Mineral. *Science and Nature*, 52(17), 493–493. <https://doi.org/10.1007/bf00646572>
- Strunz, H., Geier, B. H., & Seeliger, E. (1958). Gallit, CuGaS<sub>2</sub>, das erste selbständige Galliummineral, und seine Verbreitung in den Erzen der Tsumeb- und Kipushi-Mine. *Neues Jahrbuch für Mineralogie - Monatshefte*, 241.
- Sun, P., Niu, Y., Guo, P., Ye, L., Liu, J., & Feng, Y. (2017). Elemental and Sr–Nd–Pb isotope geochemistry of the Cenozoic basalts in Southeast China: Insights into their mantle sources and melting processes. *Lithos*.
- Sun, S. S. (1982). Chemical composition and origin of the earth's primitive mantle. *Geochimica et Cosmochimica Acta*, 46(2), 179–192. [https://doi.org/10.1016/0016-7037\(82\)90245-9](https://doi.org/10.1016/0016-7037(82)90245-9)
- Sylvester, P. J., Simon, S. B., & Grossman, L. (1993). Refractory inclusions from the Leoville, Efremovka, and Vigarano c3v chondrites: Major element differences between types A and B, and extraordinary refractory siderophile element compositions. *Geochimica et Cosmochimica Acta*, 57(15), 3763–3784. [https://doi.org/10.1016/0016-7037\(93\)90154-o](https://doi.org/10.1016/0016-7037(93)90154-o)
- Tanaka, A. (2004). Toxicity of indium arsenide, gallium arsenide, and aluminium gallium arsenide. *Toxicology and Applied Pharmacology*, 198(3), 405–411. <https://doi.org/10.1016/j.taap.2003.10.019>
- Tandon, S. N., & Wasson, J. T. (1968). Gallium, germanium, indium and iridium variations in a suite of L-group chondrites. *Geochimica et Cosmochimica Acta*, 32(10), 1087–1109. [https://doi.org/10.1016/0016-7037\(68\)90109-9](https://doi.org/10.1016/0016-7037(68)90109-9)
- Teng, F. Z., Li, W. Y., Rudnick, R. L., & Gardner, L. R. (2010). Contrasting lithium and magnesium isotope fractionation during continental weathering. *Earth and Planetary Science Letters*, 300(1), 63–71. <https://doi.org/10.1016/j.epsl.2010.09.036>
- Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51(7), 844–851. <https://doi.org/10.1021/ac50043a017>
- Tipper, E. T., Bickle, M. J., Galy, A., West, A. J., Pomiès, C., & Chapman, H. J. (2006). The short term climatic sensitivity of carbonate and silicate weathering fluxes: Insight from seasonal variations in river chemistry. *Geochimica et Cosmochimica Acta*, 70(11), 2737–2754. <https://doi.org/10.1016/j.gca.2006.03.005>
- Trenberth, K. E., Smith, L., Qian, T., Dai, A., & Fasullo, J. (2007). Estimates of the global water budget and its annual cycle using observational and model data. *Journal of Hydrometeorology*, 8(4), 758–769. <https://doi.org/10.1175/jhm600.1>
- Turton, A., & Mulcahy, M. (1962). *The chemistry and mineralogy of lateritic soils in the south-west of Western Australia*. Commonwealth Scientific and Industrial Research Organization.
- Uzumasa, Y., & Nasu, T. (1960). Chemical investigations of hot springs in Japan. LVII. Geochemical study of gallium in hot springs. *Nippon Kagaku Zasshi*, 81(5), 732–736. [https://doi.org/10.1246/nikkashi1948.81.5\\_732](https://doi.org/10.1246/nikkashi1948.81.5_732)
- Vanlaningham, S., Piasis, N. G., Duncan, R. A., & Clift, P. D. (2009). Glacial–interglacial sediment transport to the Meiji Drift, north-west Pacific Ocean: Evidence for timing of Beringian outwashing. *Earth and Planetary Science Letters*, 277(1–2), 64–72. <https://doi.org/10.1016/j.epsl.2008.09.033>
- Vasyukova, E. V., Pokrovsky, O. S., Viers, J., Oliva, P., Dupré, B., Martin, F., & Candaudap, F. (2010). Trace elements in organic- and iron-rich surficial fluids of the boreal zone: Assessing colloidal forms via dialysis and ultrafiltration. *Geochimica et Cosmochimica Acta*, 74(2), 0–468. <https://doi.org/10.1016/j.gca.2009.10.026>
- Vershkovskaya, O. V., & Fabrikova, E. A. (1957). *Gallium in sphalerite Geochemistry (USSR)* (p. 377).
- Viers, J., Dupré, B., & Gaillardet, J. (2009). Chemical composition of suspended sediments in World Rivers: New insights from a new database. *The Science of the Total Environment*, 407(2), 853–868. <https://doi.org/10.1016/j.scitotenv.2008.09.053>
- Vinogradov, I. (1935). *New estimates for Weyl sums*. (pp. 195–198). Dokl. Akad. Nauk SSSR.
- Vorobyev, S. N., Pokrovsky, O. S., Kolesnichenko, L. G., Manasyapov, R. M., Shirokova, L. S., Karlsson, J., & Kirpotin, S. N. (2019). Biogeochemistry of dissolved carbon, major, and trace elements during spring flood periods on the Ob River. *Hydrological Processes*, 33(11), 1579–1594. <https://doi.org/10.1002/hyp.13424>



- Voyer, R. A., & Modica, G. (1990). Influence of salinity and temperature on acute toxicity of cadmium to *Mysidopsis Bahía Molenock*. *Archives of Environmental Contamination and Toxicology*, 19(1), 124–131. <https://doi.org/10.1007/bf01059820>
- Wai, C. M., & Wasson, J. T. (1977). Nebular condensation of moderately volatile elements and their abundances in ordinary chondrites. *Earth and Planetary Science Letters*, 36(1), 1–13. [https://doi.org/10.1016/0012-821x\(77\)90182-0](https://doi.org/10.1016/0012-821x(77)90182-0)
- Wai, C. M., & Wasson, J. T. (1979). Nebular condensation of Ga, Ge and Sb and the chemical classification of iron meteorites. *Nature*, 282(5741), 38–39. <https://doi.org/10.1038/282790a0>
- Wang, Z., Ma, J., Li, J., Zeng, T., & Wei, G. (2020). Effect of Fe–Ti oxides on Mo isotopic variations in lateritic weathering profiles of basalt. *Geochimica et Cosmochimica Acta*, 286, 380–403. <https://doi.org/10.1016/j.gca.2020.07.030>
- Wasson, J., & Kallemeyn, G. (2002). The IAB iron-meteorite complex: A group, five subgroups, numerous grouplets, closely related, mainly formed by crystal segregation in rapidly cooling melts. *Geochimica et Cosmochimica Acta*, 66(13), 2445–2473. [https://doi.org/10.1016/s0016-7037\(02\)00848-7](https://doi.org/10.1016/s0016-7037(02)00848-7)
- Wasson, J., & Richardson, J. (2001). Fractionation trends among IVA iron meteorites: Contrasts with IIIAB trends. *Geochimica et Cosmochimica Acta*, 65(6), 951–970. [https://doi.org/10.1016/s0016-7037\(00\)00597-4](https://doi.org/10.1016/s0016-7037(00)00597-4)
- Wasson, J. T. (1967a). Concentrations of Ni, Ga, and Ge in a series of Canyon Diablo and Odessa meteorite specimens. *Journal of Geophysical Research*, 72(2), 721–730. <https://doi.org/10.1029/jz072i002p00721>
- Wasson, J. T. (1967b). The chemical classification of iron meteorites: I. A study of iron meteorites with low concentrations of gallium and germanium. *Geochimica et Cosmochimica Acta*, 31(2), 161–180. [https://doi.org/10.1016/s0016-7037\(67\)80043-7](https://doi.org/10.1016/s0016-7037(67)80043-7)
- Wasson, J. T. (1999). Trapped melt in IIIAB irons; solid/liquid elemental partitioning during the fractionation of the IIIAB magma. *Geochimica et Cosmochimica Acta*, 63(18), 2875–2889. [https://doi.org/10.1016/s0016-7037\(99\)00283-5](https://doi.org/10.1016/s0016-7037(99)00283-5)
- Wasson, J. T., & Choe, W.-H. (2009). The IIG iron meteorites: Probable formation in the IIB core. *Geochimica et Cosmochimica Acta*, 73(16), 4879–4890. <https://doi.org/10.1016/j.gca.2009.05.062>
- Wasson, J. T., Huber, H., & Malvin, D. J. (2007). Formation of IIB iron meteorites. *Geochimica et Cosmochimica Acta*, 71(3), 760–781. <https://doi.org/10.1016/j.gca.2006.09.032>
- Webb, D. R., Sipes, I. G., & Carter, D. E. (1984). In vitro solubility and in vivo toxicity of gallium arsenide. *Toxicology and Applied Pharmacology*, 76(1), 96–104. [https://doi.org/10.1016/0041-008x\(84\)90032-2](https://doi.org/10.1016/0041-008x(84)90032-2)
- Wedepohl, K. H. (1969). *Handbook of geochemistry*.
- Weissberg, B. G., Browne, P. R., & Seward, T. M. (1979). Ore metals in active geothermal systems. In *Geochemistry of hydrothermal ore deposits* (pp. 738–780).
- Welch, S. A., Green, E. G., & Banfield, J. F. (2004). *Geochemistry and biogeochemistry of Ga, Ge, and Ti during weathering* (pp. A146–A146). V M Goldschmidt Conference.
- Wheeler, D. M., & Power, I. L. (1995). Comparison of plant uptake and plant toxicity of various ions in wheat. *Plant and Soil*, 172(2), 167–173. <https://doi.org/10.1007/bf00011318>
- Whitmore, L. M., Pasqualini, A., Newton, R., & Shiller, A. M. (2020). Gallium: A new tracer of Pacific water in the Arctic Ocean. *Journal of Geophysical Research: Oceans*, 125(7). <https://doi.org/10.1029/2019jc015842>
- Wimpenny, J., Marks, N., Knight, K., Borg, L., Ryerson, R., & Ryerson, F. (2020). Constraining the behavior of gallium isotopes during evaporation at extreme temperatures. *Geochimica et Cosmochimica Acta*, 286, 54–71. <https://doi.org/10.1016/j.gca.2020.07.006>
- Wolfenden, E. B. (1965). Geochemical behaviour of trace elements during bauxite formation in Sarawak, Malaysia. *Geochimica et Cosmochimica Acta*, 29(9), 1051–1062. [https://doi.org/10.1016/0016-7037\(65\)90102-x](https://doi.org/10.1016/0016-7037(65)90102-x)
- Wood, S. A., & Samson, I. M. (2006). The aqueous geochemistry of gallium, germanium, indium and scandium. *Ore Geology Reviews*, 28(1), 57–102. <https://doi.org/10.1016/j.oregeorev.2003.06.002>
- Xiao, Y., Vocke, R., Swihart, G., & Xiao, Y. (1997). Boron volatilization and its isotope fractionation during evaporation of boron solution. *Analytical Chemistry*, 69(24), 5203–5207. <https://doi.org/10.1021/ac970621j>
- Yamamoto, T., Otsuka, Y., & Uemura, K. (1976). Gallium content in seaweeds. *Journal of the Oceanographical Society of Japan*, 32(4), 182–186. <https://doi.org/10.1007/bf02107273>
- Yamauchi, H., Takahashi, K., Yamamura, Y., & Fowler, B. A. (1992). Metabolism of subcutaneous administered indium arsenide in the hamster. *Toxicology and Applied Pharmacology*, 116(1), 66–70. [https://doi.org/10.1016/0041-008x\(92\)90145-i](https://doi.org/10.1016/0041-008x(92)90145-i)
- Yang, J.-L., & Chen, H.-C. (2003). Growth retardation and histopathology of common carp (*Cyprinus carpio*) exposed to gallium. *Bulletin of Environmental Contamination and Toxicology*, 71(2), 0240–0247. <https://doi.org/10.1007/s00128-003-0156-4>
- Yang, J.-L., & Chen, L.-H. (2018). Toxicity of antimony, Gallium, and indium toward a teleost model and a native fish species of semiconductor manufacturing districts of Taiwan. *Journal of Elementology*, 23(1)
- Yang, L., & Meija, J. (2010). Resolving the germanium atomic weight disparity using multicollector ICPMS. *Analytical Chemistry*, 82(10), 4188–4193. <https://doi.org/10.1021/ac100439j>
- Yang, S., Humayun, M., & Salters, V. J. M. (2020). Elemental constraints on the amount of recycled crust in the generation of mid-oceanic ridge basalts (MORBs). *Science Advances*, 6(26), eaba2923. <https://doi.org/10.1126/sciadv.aba2923>
- Yuan, W., Chen, J. B., Birck, J.-L., Yin, Z. Y., Yuan, S. L., Cai, H. M., et al. (2016). Precise analysis of gallium isotopic composition by MC-ICP-MS. *Analytical Chemistry*, 88(19), 9606–9613. <https://doi.org/10.1021/acs.analchem.6b02317>
- Yuan, W., Saldi, G. D., Chen, J., Zuccolini, M. V., Birck, J.-L., Liu, Y., & Schott, J. (2018). Gallium isotope fractionation during Ga adsorption on calcite and goethite. *Geochimica et Cosmochimica Acta*, 223, 350–363. <https://doi.org/10.1016/j.gca.2017.12.008>
- Zhang, T., Zhou, L., Yang, L., Wang, Q., Feng, L.-P., & Liu, Y.-S. (2016). High precision measurements of gallium isotopic compositions in geological materials by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, 31(8), 1673–1679. <https://doi.org/10.1039/c6ja00202a>
- Zheng, W., Foucher, D., & Hintelmann, H. (2007). Mercury isotope fractionation during volatilization of Hg (0) from solution into the gas phase. *Journal of Analytical Atomic Spectrometry*, 22(9), 1097–1104. <https://doi.org/10.1039/b705677j>
- Zhu, X. K., O’Nions, R. K., Guo, Y., Belshaw, N. S., & Rickard, D. (2000). Determination of natural Cu-isotope variation by plasma-source mass spectrometry: Implications for use as geochemical tracers. *Chemical Geology*, 163(1), 139–149. [https://doi.org/10.1016/s0009-2541\(99\)00076-5](https://doi.org/10.1016/s0009-2541(99)00076-5)