News & views

Planetary geochemistry

Phosphate discovery hints at chemistry of Enceladus

Mikhail Yu. Zolotov

Evidence of phosphates in the subsurface ocean of Enceladus, an icy moon of Saturn, confirms that the water is alkaline. The finding provides clues about the geochemistry and origin of this moon and its ability to support life. **See p.489**

The formation and evolution of the icy moons of giant planets are of particular interest in planetary science, because several such satellites in the Solar System could have subsurface oceans of water. These oceans are suspected to contain dissolved salts and organic matter, and might have the potential to support life. On page 489, Postberg *et al.*[1] report the detection of sodium phosphates in icy grains emitted in a plume from Enceladus, one of Saturn's moons. The finding supports the idea that the plume derives from an alkaline subsurface ocean, and suggests that Enceladus formed, in part, from a mixture of the ices of carbon dioxide and water (CO_2–H_2O ice), a constituent of comets.

The concentration of phosphorus and the occurrence of its chemical compounds in geological samples are used to constrain estimates of the physical and chemical conditions that have existed in various terrestrial and extraterrestrial sites – such as in the parent bodies of meteorites, in lunar and Martian settings, and in Earth's crust. Moreover, the presence of phosphorus compounds in water is crucial for biological productivity on Earth, and is therefore a key factor when assessing whether distant worlds have the potential to support life.

The earliest objects in the Solar System – such as parent bodies of chondrites (a type of meteorite) and possibly also comets – commonly accreted mineral dust that contained iron phosphides, in which phosphorus was in the zero oxidation state[2]. Melting of accreted ice on parent bodies of chondrites caused oxidation of P(0) to P(v), thereby forming poorly soluble calcium phosphates that precipitate out of solution. Likewise, phosphate ions in water systems on Earth are usually scarce owing to the low solubility of calcium phosphates. However, the concentrations of dissolved phosphates are elevated in calcium-poor waters, which favour the dissolution of calcium phosphates.

Soda lakes on Earth (which contain high concentrations of dissolved sodium, carbonate and bicarbonate ions) have low levels of dissolved calcium because calcium ions become sequestered in calcium carbonate minerals in these waters[3,4]. The abundant phosphate ions in soda lakes can therefore be attributed to the low concentration of calcium ions relative to sodium ions[4]. It has been suggested that phosphates would also have been abundant in alkaline carbonate-rich lakes that might have formed on early Earth[4]. Similarly, the subsurface oceans of icy moons might be rich in phosphates if the waters are like those of soda lakes.

What clues are there about the chemistry of the subsurface ocean on the ice-covered moon Enceladus? Exploration of Enceladus by the Cassini spacecraft led to the discovery of a permanent plume of gases and icy grains emitted from fissures in the icy shell. Cassini's *in situ* detections of sodium salts (chloride, carbonate and bicarbonate) in the icy grains, together with water and CO_2 in the plume gases, have been interpreted as evidence of an alkaline subsurface ocean of water that contains sodium, chloride, carbonate and bicarbonate ions, and which is boiling at low pressure[5–8]. The inferred concentrations of the ions in Enceladus's ocean have been used to deduce that dissolved phosphates are abundant in that ocean[9].

Postberg *et al.* now identify sodium phosphates in mass spectra of the icy grains in Enceladus's plume, recorded by Cassini's Cosmic Dust Analyzer (CDA) – the instrument that had previously been used to detect inorganic[5,6] and organic compounds[10] in particles sourced from the plume. The authors infer

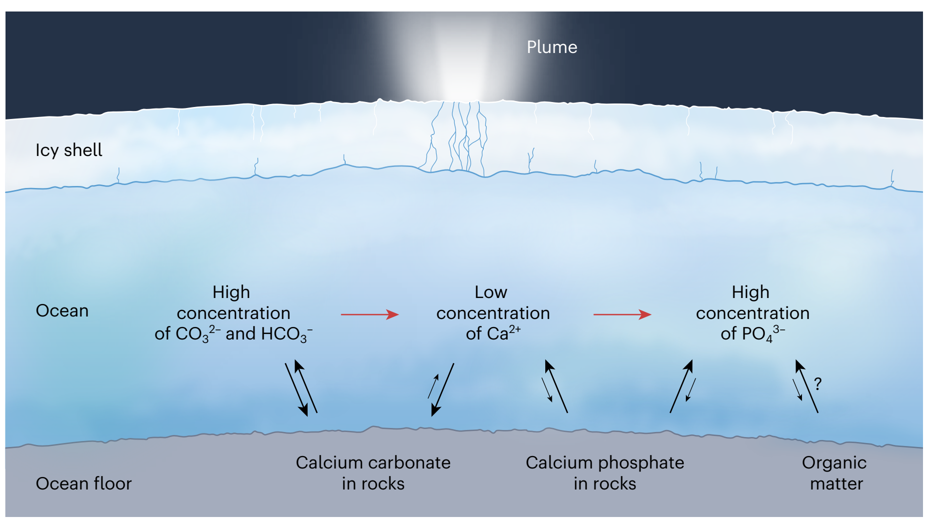

Figure 1 | Processes that affect ion concentration in Enceladus's ocean. Enceladus, a moon of Saturn, has a subsurface ocean that emits a plume of gases and icy grains through fissures in a shell of ice. Postberg *et al.*[1] report the detection of sodium phosphates in grains, which – together with previously reported detections of other salts – allowed them to propose a model of Enceladean geochemistry. High concentrations of dissolved carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions suppress the level of calcium ions (Ca^{2+}) in the water, which are in chemical equilibrium with calcium carbonate minerals. In turn, the low concentration of Ca^{2+} increases the abundance of dissolved phosphate ions (PO_4^{3-}), which are in equilibrium with calcium phosphates. In addition to the processes proposed by Postberg and colleagues, levels of dissolved phosphate might be increased by processes involving organic matter. Red arrows indicate how the concentrations of ions affect those of other ions; black arrows indicate chemical equilibria.

from their data that phosphates are indeed abundant in Enceladus's ocean, consistent with the high concentrations of carbonate and bicarbonate ions in the water.

The researchers also carried out laboratory experiments in which material from a chondrite (used as an analogue of Enceladus's rocky core) was exposed to sodium carbonate solution, and observed that the levels of dissolved phosphate increased with the carbonate content. These experiments, together with theoretical considerations put forward by Postberg and colleagues, confirmed that substantial sequestration of dissolved calcium ions into carbonate minerals favours the release of phosphate ions from calcium phosphate minerals. The results are consistent with earlier predictions of elevated dissolved phosphate levels based on modelling of the geochemistry of soda lakes on Earth[4] and of the ocean on Enceladus[9].

One factor that is not considered in Postberg and colleagues' analysis, or in the previous modelling studies[9], is whether the abundance of dissolved phosphates on Enceladus is increased by the incorporation of calcium ions into organic complexes — as has been suggested to happen in soils[11]. Another unconsidered factor is that the sodium carbonate in the ocean water would promote the desorption of phosphate ions from organic and other ocean-floor materials. This type of effect is helpful in the laboratory, where sodium carbonate solutions are used to extract soluble phosphates from soils[12]. Other limitations of the new study are that only nine phosphorus-containing icy grains have been identified in the Cassini CDA data set, and the authors had to make assumptions in their modelling to determine the composition and abundances of the phosphorus compounds. Future *in situ* investigations of the plume, or of plume materials returned to Earth, should therefore probe the details of Enceladean ocean chemistry and the identities of the phosphorus compounds.

Postberg and co-workers' discovery of phosphates in the plume of Enceladus supports the idea[5,7,9] that a soda ocean is sandwiched between the moon's icy shell and a core of rock that contains phosphate and carbonate minerals (Fig. 1). In turn, the presence of a soda ocean implies that Enceladus formed from CO_2–H_2O ices that are common in comets in the outer Solar System. If Enceladus did originate in the outer Solar System, that would suggest that, as is the case for comets[13], up to around 50% of the interior mass of the satellite is organic matter — consistent with the presence of organic compounds in the plume[10]. The new results also imply that aqueous phosphates could be abundant on other ice-covered bodies in the outer Solar System thought to have subsurface oceans, increasing the prospects of their habitability.

The discovery of sodium phosphates in the Enceladean plume lends weight to the idea that any sodium phosphates found in other extraterrestrial settings would have precipitated from soda solutions. The presence of sodium-bearing phosphates and abundant carbonates in samples returned from the asteroid Ryugu indicates that iron phosphides in the asteroid material have undergone aqueous oxidation to form phosphates[14]. Perhaps these sodium phosphates precipitated from a sodium-rich solution within Ryugu's parent body, which had formed in the outer Solar System from CO_2–H_2O ices and other materials[1,14].

Similarly, if sodium phosphates or carbonates were found in rock samples from Venus, this would suggest that soda lakes or seas once existed on the currently dry planet. This would be interesting because the sodium carbonate in such reservoirs could have formed through the sequestration of an early CO_2-rich atmosphere — and would thus provide crucial information about the enigmatic history of our sister planet. In turn, the apparent lack of sodium phosphates in rock samples from Mars does not support the idea[3] that an early dense, CO_2-rich atmosphere[15] was consumed to form soda solutions and corresponding salts.

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Ancient DNA

Onset of farming in northwest Africa traced

Louise Humphrey & Abdeljalil Bouzouggar

Genomic data from bones and teeth found at archaeological sites across Morocco paint a picture of how Neolithic farmers and pastoralists spread into northwest Africa that is more complex than previously thought. **See p.550**

The shift in human cultures from hunter-gatherer lifestyles to those based on the cultivation and husbandry of domesticated plants and animals is known as the Neolithic or agricultural transition. How Neolithic lifestyles spread into northwest Africa has been unclear, with archaeological findings providing conflicting evidence for both the migration of farmers into the area (demic diffusion) and the adoption of a Neolithic lifestyle by local foraging groups (cultural diffusion)[1]. Ancient human DNA could help to settle the debate. On page 550, Simões *et al.*[2] describe human genomic data from three previously unsampled archaeological sites in Morocco, dated to between 7,600 and 5,700 years ago — around the time when farming became established in the region[3]. The data provide an opportunity to refine and expand previous perspectives on the arrival and spread of Neolithic and pastoralist lifestyles in Morocco.

Previously, genomic data had been recovered only from three prehistoric sites in Morocco[4,5]. The oldest site, Taforalt — a cave in northeastern Morocco that houses an ancient cemetery — dates to close to the end of the last glacial period, about 14,500 years ago[4]. The DNA obtained at this site came from seven people belonging to a group called Iberomaurusian hunter-gatherers. The analysis revealed ancestry related to both sub-Saharan African groups and hunter-gatherer populations from the Levant (an area bordering the eastern Mediterranean that encompasses the land bridge between western Africa and Eurasia).

The second site, Ifri n'Amr o'Moussa in western Morocco, yielded DNA dating to about 7,000 years ago[5]. These early Neolithic