The distribution of iodide and iodate in anchialine cave waters — Evidence for sustained localised oxidation of iodide to iodate in marine water

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ARTICLE INFO

ABSTRACT

A study of inorganic iodine speciation in the waters of seven Croatian coastal caves is described. These are anchialine caves as they are connected hydraulically with Adriatic Sea surface water, with the tide inside the cave rising and falling with that outside, but replenishment of the water is restricted by the karst rock. In effect, the water in the cave probably acts more like a piston, and although moving slightly vertically, has a long residence time compared to a fully-flushing cave. Anchialine environments display a number of unusual features, e.g., a well-developed pycnocline, hypoxia and endemic fauna. Iodate and iodide were determined by differential pulse voltammetry and cathodic stripping square wave voltammetry, respectively. Low iodide concentrations (<10 nM) have been consistently identified in the bottom water of the caves where concentrations of 90–100 nM would ordinarily be expected from intrusion of Eastern Adriatic surface seawater. Where total inorganic iodine concentrations behave conservatively with salinity the loss of the iodide implies oxidation to iodate. As iodide oxidation remains one of the enduring academic problems of the marine iodine system the study of iodine in anchialine caves may help unravel it. Iodate reduction was observed in mid-water, at the halocline, and mechanisms for the reduction involving either respiration or chemolitho-autotrophic bacteria are considered. The respiration mechanism is favoured because of enhanced alkalinity found in the near surface waters of the caves.

1. Introduction

In oxic seawater dissolved iodine is present as iodate and iodide, at a total concentration of about 450 nM (e.g., Tsunogai and Henmi, 1971; Tian and Nicolas, 1995; Campos et al., 1996; Truesdale et al., 2000). In deep-ocean waters the iodine system approaches thermodynamic equilibrium (Sillen, 1961), with iodate predominating (Tsunogai and Sase, 1969); iodide concentrations are generally lower than 10 nM, probably resulting from iodine re-mineralising from sinking detritus (Luther et al., 1988; Wong, 1991; Truesdale, 1994a). Meanwhile, tropical and sub-tropical ocean surface waters and temperate shelf seas contain iodide concentrations comparable to those of iodate (Elderfield and Truesdale, 1980; Wong and Zhang, 1992; Truesdale, 1994b; Campos et al., 1996). Particulate iodine is present in ocean waters at pM concentrations (Wong et al., 1976). Dissolved organic-I is present at low concentrations in open ocean waters but can attain concentrations of ~100 nM in near-shore environments (Truesdale, 1975; Luther and Cole, 1988; Luther et al., 1991; Cook et al., 2000; Wong and Cheng, 2001; Wong and Zhang, 2003). In anoxic systems, e.g., the Black Sea, deep trenches, and some mid-water oxygen minimum zones, iodide is the

thermodynamically favoured form and iodate is essentially absent (Wong et al., 1985; Luther and Campbell, 1991; Farrenkopf et al., 1997).

Although most work on iodine redox dynamics in oxic waters has focussed upon the phytoplanktonic reduction of iodate in the photic layer of the ocean the evidence for this remains controversial. Some report that dense algal cultures reduce iodate (Sugawara and Terada, 1967; Moisan et al., 1994; Wong et al., 2002; Chance et al., 2007), while others only find that it happens at higher than ambient iodate concentrations (Waite and Truesdale, 2003), or insignificantly (Truesdale, 1978; Butler et al., 1981). Sugawara and Terada (1967) suggested that iodate is so close in structure to nitrate that it could be reduced by processes reducing nitrate, prior to nitrogen assimilation by algae. Further, Nitrate Reductase was hypothesised as the enzyme responsible, especially when nitrate concentrations have decreased, and competition between iodate and nitrate thereby increases. This suggestion was criticised by Truesdale and Bailey (2002) who used Michaelis–Menten kinetics to demonstrate that competition between nitrate and iodate will barely change as nitrate concentrations decrease. Further, Waite and Truesdale (2003) showed that iodate reduction (at higher than ambient concentrations) was unaffected when NR activity was 'switched off' by growing the alga in culture containing tungsten rather than molybdenum.

In addition to the above, mesocosm experiments and hydrographic studies in polar and temperate waters have not demonstrated any

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significant reduction of iodate during periods equivalent to the spring algal bloom (Truesdale, 1978, 1994b; Truesdale and Jones, 2000; Truesdale et al., 2003). Campos et al. (1996) and Tian et al. (1996) have both suggested that iodate reduction in warm ocean waters may be a function of regenerated production (that depending upon ammonium) rather than new production (that depending upon nitrate). Wong (2001) re-interpreted this same information suggesting that iodate is reduced in direct relationship to nitrate uptake. Truesdale and Bailey (2002) suggest instead that iodate reduction might depend upon bacterial action in respiration, rather than algae in primary production. Finally, recognising the broad zonal correlation between sunlight exposure and iodate reduction Spokes and Liss (1996) investigated the photochemical reduction of iodate, initiated by organic matter. As with the phytoplankton experiments this produced somewhat uncertain results. Truesdale (2007) demonstrated that at natural concentrations in seawater, the photochemical reduction of iodate by iodide could not account for the extent of iodate reduction in surface seawaters. Meanwhile, Truesdale and Upstill-Goddard (2003) considered that in shallow coastal zones tidal-currents may inject water into the sedimentary anoxic zone, where iodate could be reduced by reaction with sulfide (Zhang and Whitfield, 1986). The hypothesis seems to be supported by Hou et al. (2007) who used ^{129}I as a radiogenic tracer in the North Sea and English Channel, and who report inter-conversion of $^{129}IO_3^-$ to $^{129}I^-$ in relatively shallow areas.

Iodide oxidation is even more elusive than iodate reduction. The process is thermodynamically spontaneous in oxic seawater since coupling the oxygen/hydroxide and the iodide/iodate systems of seawater together in the Nernst equation, predicts iodate to be the only analytically detectable iodine component present (Sillen, 1961). Given the vast preponderance of iodate in the deep ocean, together with the known input of particulate-I from shallower waters, some of which will mineralise to iodide (Wong, 1991; Truesdale, 1994a), iodide oxidation must occur there somewhere. Rates may be low, making laboratory demonstration and the establishment of a mechanism difficult. Indeed, calculations based upon Molecular Orbital Theory (Luther et al., 1995) imply that an abiotic mechanism is unlikely in deep water and that biotic mechanisms are still to be preferred in surface waters. From direct observation of several months' storage of large volumes of seawater entrapped below the photic zone in Loch Etive, Edwards and Truesdale (1997) report an iodide oxidation rate of about 30 nM/year. Meanwhile, using the distinctively different approach of tracking $^{129}I^-$ and $^{129}IO_3^-$ from nuclear waste, Hou et al. (2007) concluded that iodide oxidation is slow in the North Sea. In contrast, but again by direct observation, Žic and Branica (2006a) report iodide oxidation to iodate in a karst marine water body dominated by photosynthesis. Although the precise dynamics of the oxidation are not known, the amount of iodate formed in a 9 month period gives an average oxidation rate of about 550 nM/year. The water in the system is not thought to be replenished directly, so this oxidation rate is not contaminated by an advective term for iodate. As a result this observation may therefore be the most reliable evidence of iodide oxidation available so far. Other direct reports of iodide and iodate concentrations changing over hours rather than months, e.g., Beck and Bruland (2000); Brandao et al. (1994), relate to shallow embayments or estuaries, and these probably reflect transport of iodine between sediment and water, and not an oxidation or reduction actually in the water. Also, in laboratory cultures Sugawara and Terada (1967) demonstrated iodide oxidation simultaneously with iodate reduction by the diatom, *Navicula* sp. Meanwhile several workers (Gozlan, 1968; Gozlan and Margalith, 1974; Fuse et al., 2003; Amachi et al., 2005a,b) have isolated particular marine bacteria in laboratory cultures, and showed that at high iodide concentration they can oxidise iodide to molecular iodine as well as form organic-I compounds. However, none of the bacteria seems to have produced iodate. In addition, iodide oxidation has been inferred by hydrographic modelling. From their model Campos et al. (1996) estimated the half-life of iodide in the surface waters of tropical gyres to be about 70 days. (Assuming

iodide concentrations of 102 and 215 nM in the Atlantic and Pacific gyres studied, this corresponds to rates of ~270 and 560 nM/year, respectively.) Similarly, using a box model Truesdale et al. (2001) deduced that iodide oxidation occurs in the intermediate waters of the Black Sea, possibly in parallel with nitrification.

This paper describes the results of a preliminary survey of the iodine distributions in seven anchialine cave environments (defined below) on the Croatian coast. Perhaps the most interesting discovery has been high iodate, low iodide concentrations in the bottom waters of the caves. These contrast markedly with the Adriatic surface water that feeds the caves, and present direct evidence of a marked localised oxidation of iodide to iodate in seawater; they are reminiscent of deep-ocean waters (Truesdale, 1994a). Iodate reduction has also been found to occur higher in the water column at the halocline. Since anchialine caves exist in many parts of the world, potentially they offer new routes to mechanisms for iodide oxidation and iodate reduction in the oceans.

2. The anchialine environment

The anchialine environment was defined at the 1984 International Congress of Marine Cave Biology, Bermuda (Stock et al., 1986) as containing bodies of haline waters, usually with a restricted exposure to open air, and always with more or less extensive subterranean connections to the sea, which show noticeable marine as well as terrestrial influences. Those of volcanic origin typically include flooded, highly porous lava tubes, but the more common ones, as in Croatia, are developed by dissolution of limestone bedrock. Cave enlargement at the halocline is important because of "mixing corrosion" wherein a mixture of fresh and saline waters, each of which is saturated with respect to calcium carbonate, is nevertheless under-saturated itself. The waters are usually stratified due to a density gradient between the upper lens of fresh or brackish water and the underlying seawater; the normal mixing due to atmospheric influences (wind, evaporative surface cooling, etc.) being damped-out by the closed nature of the cave system. Where caves are in darkness there is, of course, little or no photosynthesis, and because respiration dominates, the waters are generally under-saturated with respect to oxygen. Indirectly then, due to little, if any, surface exposure, chemo-synthetic micro-organisms play a major role in the food-web. Occasionally, input of even small amounts of terrestrial organic material, whether natural or anthropogenic, together with a restricted water exchange, results in anoxia and a sulfidic environment that usually extends around the halocline (Iliffe et al., 1984; Sket, 1986, 1996; Humphreys, 1999). This is also a zone of a pH minimum, and the increased acidity at the halocline accelerates the dissolution of limestone often resulting in cave passages at this depth (Iliffe and Bishop, 2007). The geomorphology, extreme physico-chemical conditions and food paucity in these environments control the specific type of biota in a given system, often rich in endemic species. Some marine troglobites are closely related to deep sea species, while some are "living fossils" which show Tethyan distribution (Iliffe et al., 1983; Iliffe, 1986, 1992; Sket, 1996).

3. The anchialine caves studied

The eastern coast of the Adriatic Sea (Fig. 1) is a karst region characterized by porous limestone and semi-porous dolomites with some flysch, an impervious, thin-layered sedimentary rock, as hydraulic barriers. Bjejajka Cave and Lenga Pit (Table 1) are anchialine objects located in the National Park Mljet, on the Island of Mljet. The investigation of them started seven years ago by the members of the Croatian Biospeleological Society (Ozimec, 2002, 2003). Both are situated about 100 m from the sea coast and are cut in late Jurassic and early Cretaceous dolomites with limestone lenses.

Lenga Pit is a 22 m deep vertical pit of which one half is dry, and is directly open to the atmosphere through a relatively narrow opening