







A new method for extracting conodonts and radiolarians from chert with NaOH solution

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Abstract: Microfossils are important components of sedimentary rocks used for palaeontological, biostratigraphic, palaeoenvironmental and palaeoclimatic investigations. They are usually extracted from rocks using an acid solution, which might vary depending on the embedding rock lithology. Here we propose a new method using common NaOH (sodium hydroxide; soda) to digest cherts (micro- and cryptocrystalline quartz) instead of the standard technique based on HF (hydrofluoric acid). This new method allows the collection of

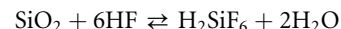
undamaged specimens of different kinds of microfossils, such as conodonts, radiolarians, teeth and dermal scales, the mineralogy of which is still preserved (e.g. biogenic apatite in conodonts). The use of soda is thus recommended, as it is less dangerous, less expensive, and it better preserves the extracted microfossils both in shape and mineralogy.

Key words: chert, soda, conodont, radiolarian, chemical method, dissolution technique.

CONODONTS are small elements of the feeding apparatus of a marine eel-like organism that lived in the Palaeozoic to Lower Jurassic oceans (Du *et al.* 2020). They consist of platforms, cones and blades, and are composed of hydroxyfluorapatite [$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{F}, \text{OH})$]. Conodonts are very difficult to see in the field with a lens, even though their dimensions can reach up to a few millimetres (range: 100 μm to 4 mm). To study conodonts, rocks of different lithologies are thus collected and then disaggregated in the laboratory using various chemicals, without damaging the fossils. The residues are successively inspected with a stereoscopic microscope to pick up all the extracted microfossils. Along with conodonts, radiolarians are the most common fossils preserved and collected after the chemical digestion of the rock samples. Radiolarians are unicellular protists originally made of opaline silica, but usually collected from rocks after being replaced by calcite, pyrite, quartz and chalcedony.

Usually, conodonts are recovered from shales, marls and, in particular, limestones. In fact, the dissolution of carbonate rocks by using dilute organic acetic and formic acids, with a concentration between 20% and 7%, refresh every 20–24 hr, results in a significant increase in

conodont recovery from undissolved residues. Conodonts are in fact safe from dissolution with pH solution values above 3.6 (Jeppsson & Anehus 1995). As with radiolarians, conodonts have long been extracted from Palaeozoic and Mesozoic radiolarian cherts (Hayashi 1968, 1969, Isozaki & Matsuda 1982), and they are usually extracted using a solution of 5–15% cold hydrofluoric acid (HF), refresh every 5–24 hr (Hayashi 1969). The dissolution reaction of HF on silica (quartz) is expressed as:



Since the equilibrium constant for the dissolution reaction with HF at room temperature (25°C) is high (3.4×10^6 ; Liang & Readey 1987), silica is extremely soluble in HF solutions even at room temperature. However, the surface of the conodonts appears to be poorly preserved, having been damaged and consumed by the reaction of biogenic apatite (hydroxyfluorapatite) with inorganic HF.

Silica (SiO_2) is known to show high solubility in high pH solutions (Knauss & Wolery 1988; Brady & Walther 1990; House & Orr 1992). Sodium hydroxide (NaOH) solution has been used to dissolve siliceous ooze (Müller

& Schneider 1993; Koning *et al.* 2002; Iwasaki *et al.* 2014) based on the following reaction equation:



Experiments with silicate minerals have shown that this reaction is very slow at room temperature. For example, Choquette *et al.* (1991) reported that chert and quartz showed no evidence of reaction after immersion in NaOH solution (1 M) at 23°C for 265 days. For this reason, the dissolution of radiolarian cherts with NaOH solution has never been used. However, the solubility of NaOH solution in quartz increases significantly with increasing temperature (Choquette *et al.* 1991; Crundwell 2017; Febriana *et al.* 2020). We therefore decided to extract conodonts using the base NaOH at higher temperatures.

In this study, we successfully extracted conodonts from Triassic radiolarian chert from Japan by varying the concentration and temperature conditions of the NaOH solution. We present here a new extraction method for collecting conodonts from radiolarian cherts, which preserves the original characteristics and mineralogy. Furthermore, our study has shown that this method is useful for extracting not only conodonts, but also radiolarians and other microfossils (teeth, dermal scales) without damaging the microfossils.

METHOD

We selected chert samples from the Triassic–Jurassic boundary (TJB) chert section in the Jurassic accretionary complexes from the Mino Belt in central Japan (Hori 1992; Carter & Hori 2005; Du *et al.* 2020, 2023). This section consists mainly of rhythmic brick-red bedded cherts with a thickness of 4 m that accumulated in a pelagic, open ocean setting within a low-latitude zone of the Panthalassa Ocean (Ando *et al.* 2001). The samples used in this study are from the same chert beds previously investigated by Du *et al.* (2020, 2023), which are enriched in conodonts and radiolarians.

We washed, dried, and broke the chert sample into fragments using a pestle and mortar; then we used sieves to separate these fragments into two subsamples, divided by size: one above and one below 1 mm. For this experiment we also decided to exclude pieces larger than 10 mm. However, this method is applicable to any dimension of chert fragments. Care was taken at each step of this process to avoid any possible contamination. We placed 15 g of each subsample (<1 mm and 1–10 mm) into different NaOH solutions of 2, 3, 4 and 5 M for multiples of 24 hr (24, 48, 72, 96 and 120 hr), and then we left the sample reacting with the solutions in an oven

at two different temperatures: 50 and 80°C. Choquette *et al.* (1991) suggested using 80°C to dissolve chert and quartz using soda, and since the dissolution would take more than 260 days at 23°C (room temperature), a mean temperature of 50°C was thus selected to verify the reaction. We used simple plastic 100 ml cannisters with a screw and seal lid, that could resist up to 120°C. After reaction, we thoroughly but gently rinsed the two size subsamples (<1 mm, 1–10 mm) from each solution, and then dried the residues in an oven at 40°C. We then weighed the undissolved fraction and calculated the percentage dissolution (Table 1). The dry residues were then checked under a stereomicroscope to collect microfossils. Heavy liquid separation was not needed to concentrate the conodont-bearing residue. Rock samples and microfossils are housed at the Department of Geosciences, University of Padova (Italy).

Preservation of conodonts extracted from chert by the traditional HF method (Hayashi 1969) and the NaOH method in this study was compared using a scanning electron microscope (SEM, HITACHI TM3030 Plus) at Kyushu University, Fukuoka, Japan. The conodonts used for comparison were extracted with NaOH at a concentration of 3 M for 72 hr at 80°C. The elemental compositions of the conodonts were determined by energy dispersive x-ray spectroscopy (EDS, Bruker Quantax at Kyushu University) at an accelerating voltage of 15 kV. Quantitative analysis was performed using a Quantax 70 software. The mineralogical composition of conodonts extracted with NaOH and HF methods was analysed using a Micro-Raman Witec alpha 300 R equipped with Zeiss microscope, at the Department of Geosciences, University of Padova. The analyses were carried out by using 20 s of integration time and 10 accumulations, and a power of 10 mW.

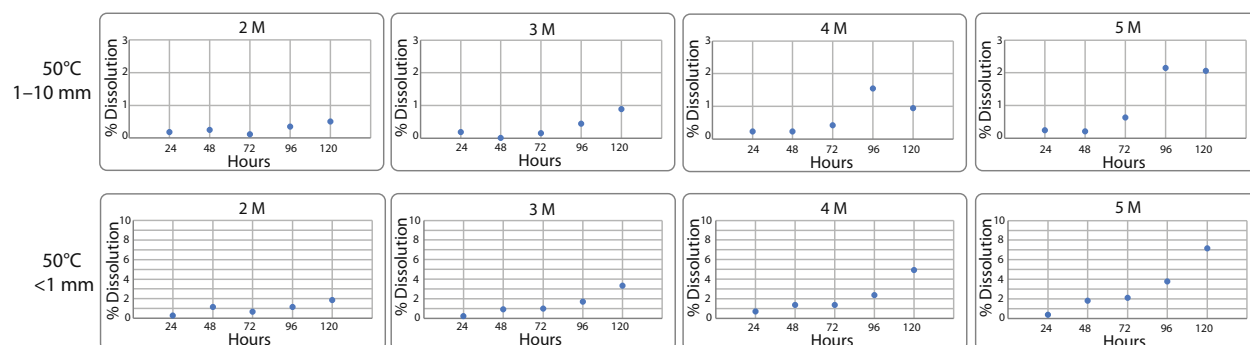
RESULTS

As expected, the percentage of dissolution of the two size subsamples is directly proportional to the timing and the molarity, at both 50 and 80°C, with some exemptions.

At 50°C, neither of the subsamples show any significant increase in dissolution for the first 72 hr: around 0.2% for fragments 1–10 mm and 2% for those <1 mm, independent of the molar concentration. After 3 days (72 hr), a significant variation in dissolution is recorded at 4M and 5M for the 1–10 mm subsample, reaching a dissolution of one order of magnitude larger compared to the shorter reaction, up to 2%. It is noteworthy that no variation of dissolution at 5 M is recorded between 96 and 120 hr (2.15% vs 2.06%), while a low decrease in dissolution percentage, from 1.55% to 0.95%, is registered for the 4 M solution at 120 hr (Fig. 1).

TABLE 1. Results of the dissolution of chert fragments (1–10 mm and <1 mm) using NaOH at 2, 3, 4 and 5 molar concentration, for 24, 48, 72, 96 and 120 hr at 50°C and 80°C.

Temp 50°C				Temp 80°C			
<1 mm		1–10 mm		<1 mm		1–10 mm	
2 M		2 M		2 M		2 M	
Time (hr)	% Dissolution	Time (hr)	% Dissolution	Time (hr)	% Dissolution	Time (hr)	% Dissolution
24	0.26	24	0.18	24	7.80	24	9.34
48	1.17	48	0.25	48	28.28	48	19.00
72	0.68	72	0.11	72	59.02	72	42.10
96	1.16	96	0.35	96	14.69	96	10.33
120	1.87	120	0.51	120	39.77	120	24.50
3 M		3 M		3 M		3 M	
Time (hr)	% Dissolution	Time (hr)	% Dissolution	Time (hr)	% Dissolution	Time (hr)	% Dissolution
24	0.26	24	0.19	24	10.80	24	10.47
48	0.90	48	0.01	48	44.36	48	25.14
72	1.00	72	0.16	72	77.73	72	51.51
96	1.71	96	0.44	96	32.90	96	22.86
120	3.33	120	0.89	120	50.32	120	44.65
4 M		4 M		4 M		4 M	
Time (hr)	% Dissolution	Time (hr)	% Dissolution	Time (hr)	% Dissolution	Time (hr)	% Dissolution
24	0.30	24	0.23	24	11.83	24	14.11
48	1.36	48	0.23	48	54.62	48	26.19
72	1.35	72	0.42	72	79.15	72	54.75
96	2.38	96	1.55	96	46.98	96	28.80
120	4.94	120	0.95	120	66.11	120	54.07
5 M		5 M		5 M		5 M	
Time (hr)	% Dissolution	Time (hr)	% Dissolution	Time (hr)	% Dissolution	Time (hr)	% Dissolution
24	0.34	24	0.24	24	15.66	24	14.29
48	1.83	48	0.21	48	70.01	48	38.89
72	2.09	72	0.63	72	82.19	72	62.60
96	3.80	96	2.15	96	50.68	96	38.19
120	7.16	120	2.06	120	66.80	120	59.40

**FIG. 1.** Graphs of the dissolution of chert fragments 1–10 mm and <1 mm using NaOH at 2, 3, 4 and 5 M concentration, for 24, 48, 72, 96 and 120 hr at 50°C.

At 80°C, both the subsamples present a dissolution of between 7% and 15% after 24 hr, depending on the molar concentration. However, the dissolved fraction increased significantly after 48 and the 72 hr, reaching values of between *c.* 40% and 60% for the larger 1–10 mm fragments, or even 60% and 80% for the subsample consisting of fragments <1 mm.

Unexpectedly, at 80°C we documented a strong decrease in dissolution in both subsamples at 2, 3, 4 and 5 molar concentration, sometimes more than 50% when compared with the results after 72 hr (Fig. 2).

The preservation of conodonts extracted from cherts using HF is directly related to the time that the microfossils remain in contact with the dissolving solution. The more conodonts are exposed to HF, the worse is the preservation, because the acid solution keeps on reacting with the fossil mineralogy. When using the NaOH solution, no variation was found between the preservation of conodonts and radiolarians collected after 24 and 120 hr, independent of the molarity and temperature, confirming that the solution preferentially attacks the rock matrix and that the solution is insufficient to affect the preservation of the fossil minerals. However, we were surprised to find that cold HF acid at 5% used for 4 hr to dissolve chert rapidly, replaced the conodont bioapatite [$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{F}, \text{OH})$] with fluorite (CaF_2), maintaining the lamellar structures typical of conodont elements (Fig. 3).

SEM images compare conodonts extracted by the HF method reported by Du *et al.* (2020) with those extracted by the NaOH method (3 M, 80°C, 72 hr) in this study (Fig. 3). The specimens consist of Rhaetian conodonts belonging to the genus *Misikella*. Many microcracks and fractures were developed in the conodonts using the HF method (Fig. 3A–C). Additionally, some corrosion was observed on the surface of the conodonts as a result of the HF treatment (Fig. 3B). Compared to the conodonts treated with NaOH, the surface of the conodonts had a rough texture with attached quartz particles and clay

minerals (Fig. 3C, E). Parallel lamellar structures were observed in the basal cavity of both HF and NaOH specimens (Fig. 3C, F). However, it is noteworthy that the preservation of the lamellae is flawless in the conodont specimens extracted by the NaOH method (Fig. 3F).

EDS analysis revealed that the conodonts extracted by the NaOH method were mainly composed of O, Ca and P, with small amounts of F (Fig. 4B, D). The results of EDS analysis indicate that the conodonts extracted by the NaOH method are entirely composed of hydroxyfluorapatite (Table 2). The P/Ca ratios range from 0.49 to 0.67 with an average of 0.6 ± 0.1 , which is close to the ideal value of hydroxyfluorapatite [$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{F}, \text{OH})$] (P/Ca = 0.6). On the other hand, the conodonts extracted by the HF method consist mainly of F and Ca (Fig. 4A). This suggests that most conodonts originally composed of hydroxyfluorapatite were replaced by fluorite (CaF_2) by reaction with HF. Moreover, almost no P was detected. Therefore, it is likely that the P was released from the conodonts as phosphoric acid (H_3PO_4). Furthermore, small amounts of Al and Si were also detected in the HF conodonts (Fig. 4C), suggesting the presence of clay minerals on the surface of the conodonts.

We also carried out micro-Raman analyses to distinguish the mineralogical components of conodonts extracted by using both the HF and NaOH methods, which are based on their chemical bounds; the resulting spectra clearly show different peaks (Fig. 5). In particular, the main peak of the conodonts extracted with HF is at 328 cm^{-1} that corresponds to fluorite mineral. In contrast, spectra with a peak at $c. 967 \text{ cm}^{-1}$, indicating a mineralogical composition of apatite, have been obtained from conodonts extracted with NaOH. As in the EDS analysis, the micro-Raman spectra suggest that fluorite (CaF_2) completely replaced the original hydroxyfluorapatite composition of the conodonts by reaction with HF (Fig. 5).

The results of this study provide compelling evidence that the NaOH method can be used for the extraction of microfossils such as conodonts from cherts, and that

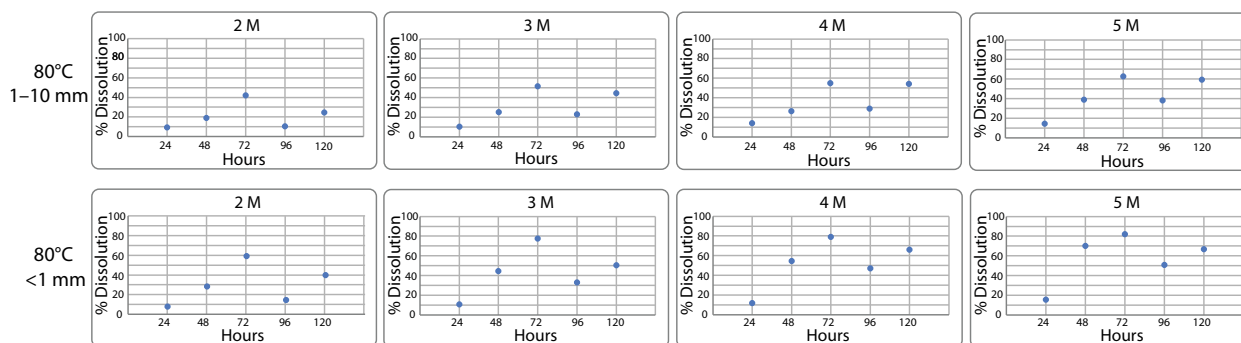


FIG. 2. Graphs of the dissolution of chert fragments 1–10 mm and <1 mm by using NaOH at 2, 3, 4 and 5 M concentration, for 24, 48, 72, 96 and 120 hr at 80°C.

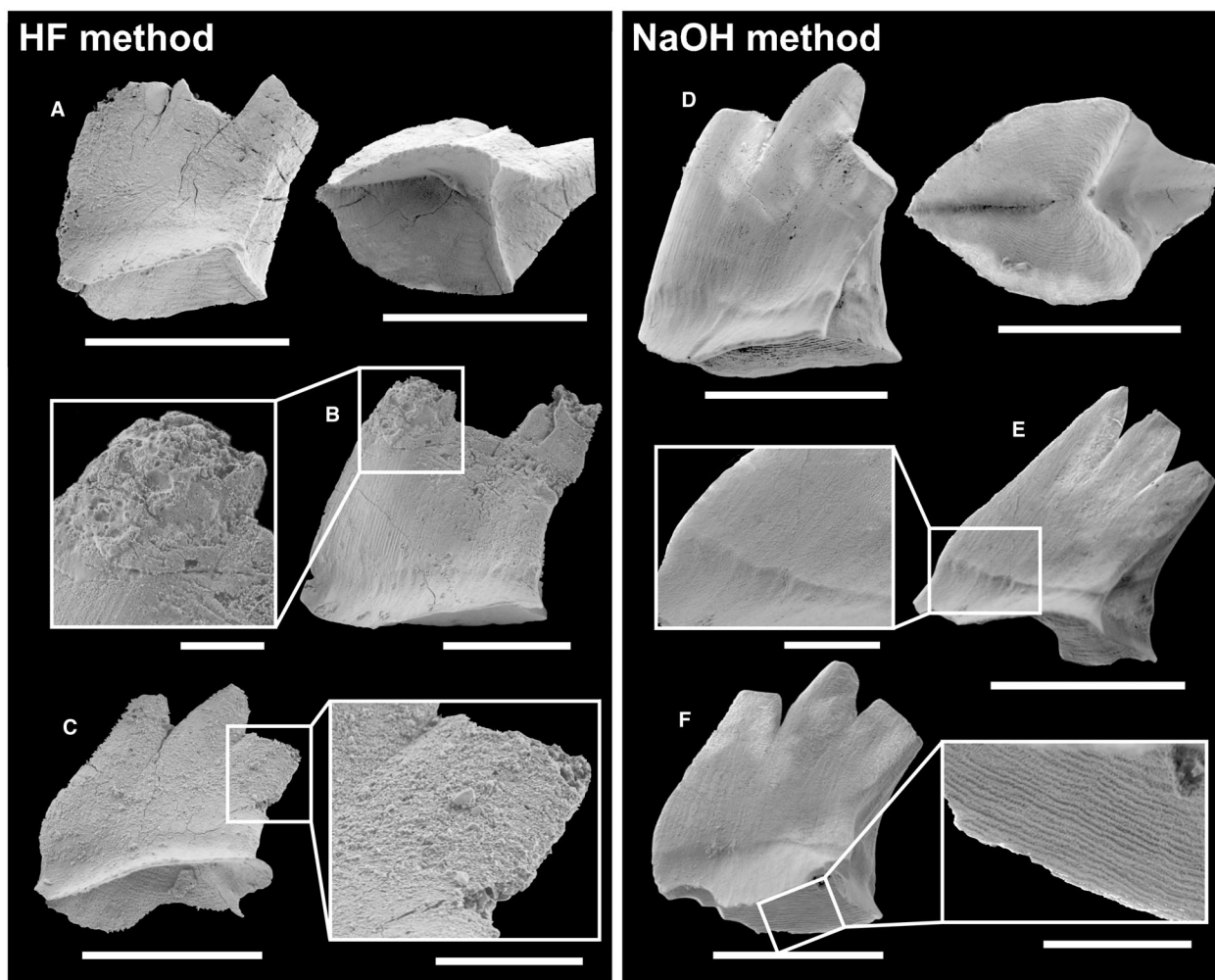


FIG. 3. Scanning electron microscope (SEM) images showing the preservation of conodonts (*Misikella posthernsteini*) extracted using HF (A–C) and NaOH (D–F). A, specimen in lateral and lower view; a faint lamellar structure remains in the basal cavity; microcracks are abundant on the conodont surface (sample HU1-1). B, significant corrosion damage is visible on the blade (HU2-47). C, compared to the specimens treated with the NaOH method (E), the conodont has a rough surface and has quartz and other clastic particles attached (sample HU2-33). D, specimen in lateral and lower view; the surface of the conodont is smooth and the lamellar structure of the basal cavity is well preserved compared to the HF method (sample HU2-47). E, sample HU2-47. F, specimen with very well-preserved lamellar structure (sample HU2-93). Scale bars represent: 100 μm (A–F); 30 μm (inset images in B, C, E, F).

conodonts retain their original composition in terms of major elements. Previous studies have used conodonts extracted from limestone using acetic/formic acid to reconstruct seawater chemistry and temperatures (e.g. Korte *et al.* 2003; Rigo & Joachimski 2010; Rigo *et al.* 2012; Callegaro *et al.* 2012; Trotter *et al.* 2015; Du *et al.* 2021). However, no similar studies have been conducted with conodonts extracted from chert using the HF method. The bedded chert sequences in the Jurassic accretionary complex in Japan have a continuous record of nearly 100 million years in a pelagic environment in the Panthalassa Ocean and are important for understanding palaeoceanographic changes in the Mesozoic and Palaeozoic. It is expected that the use of conodonts extracted by the NaOH

method will significantly increase the availability of palaeoceanographic information (e.g. palaeotemperature and redox condition) on the Panthalassa Ocean. Further studies on the analysis of isotopes (especially Sr, C and O isotopes) and on the concentrations of trace and rare earth elements are needed for the conodonts extracted using the NaOH method.

Additionally, radiolarians are a major component of chert, usually extracted with a cold HF solution (1–5% for 20–24 h) (Dumitrica 1970; Pessagno & Newport 1972). Our preliminary investigations have shown that the NaOH method can also be used to obtain radiolarians from cherts for biostratigraphic investigations. Radiolarians are originally amorphous (opal-A) when they are deposited, and

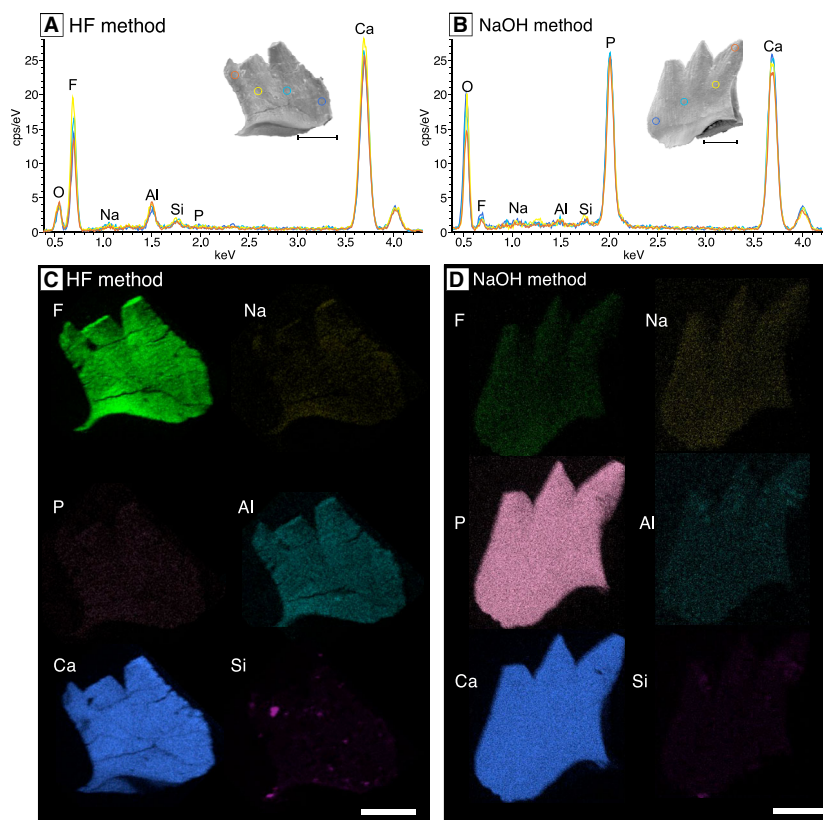


FIG. 4. X-ray energy spectra and chemical composition maps (F, Na, P, Al, Ca, Si) of the conodonts extracted by HF (A, C) and NaOH (B, D) methods. The colour of the energy spectrum corresponds to the colour of the analysed spot (10 μm) in the SEM image of the conodonts. A, transitional form between *Misikella hernsteini* and *M. posthernsteini*, sample HU2-100. B, *M. posthernsteini*, sample HU2-93. Scale bars represent 50 μm .

TABLE 2. Elemental concentrations (atomic %) from EDS analysis of 10 spots (each 10 μm) for each conodont shown in Figure 4.

Element (at %)	HU2-100, HF method		HU2-93, NaOH method	
	Mean & SD	Range	Mean & SD	Range
F	36.3 \pm 2.8	32.3–41.1	7.3 \pm 1.3	5.0–9.6
Na	0.4 \pm 0.2	0.2–0.8	0.8 \pm 0.1	0.5–1.0
Al	1.3 \pm 0.2	0.9–1.6	0.3 \pm 0.1	0.1–0.6
Si	0.5 \pm 0.2	0.3–0.9	0.3 \pm 0.1	0.1–0.5
P	0.1 \pm 0.1	bd–0.1	9.6 \pm 0.9	7.6–10.8
Ca	14.0 \pm 1.2	11.5–16.1	16.9 \pm 2.1	14.7–21.6
O	15.8 \pm 1.3	13.6–18.2	64.8 \pm 1.9	61.4–67.0
P/Ca	0.01 \pm 0.01		0.6 \pm 0.1	

then become crystalline (quartz) through diagenesis (De Wever *et al.* 2001). As a result, the siliceous sediments become chert, a hard siliceous rock. Although radiolarian shells are primarily quartz, it is unclear why individual radiolarians can be extracted using NaOH solutions. This

remains to be investigated, but at least the NaOH method can be used to safely and easily extract radiolarians and conodonts from cherts. The previous HF method requires a fume hood with a large exhaust volume, and there are regulatory restrictions on the use of HF. However, low concentrations of NaOH solutions, which are less hazardous and low cost, can be also used in educational institutions and in the geological industry. Microfossil studies using the NaOH method are expected to become popular in research institutes, schools, and companies in the near future.

CONCLUSION

We explored the use of NaOH (sodium hydroxide; soda) for the extraction of microfossils such as conodonts, radiolarians, teeth and dermal scales from fine-grained sedimentary rocks composed of microcrystalline or cryptocrystalline quartz like cherts. Comparing the different molar concentrations (2, 3, 4, 5 M), the time of reaction (24, 48, 72, 96, 120 hr) and the percentage of

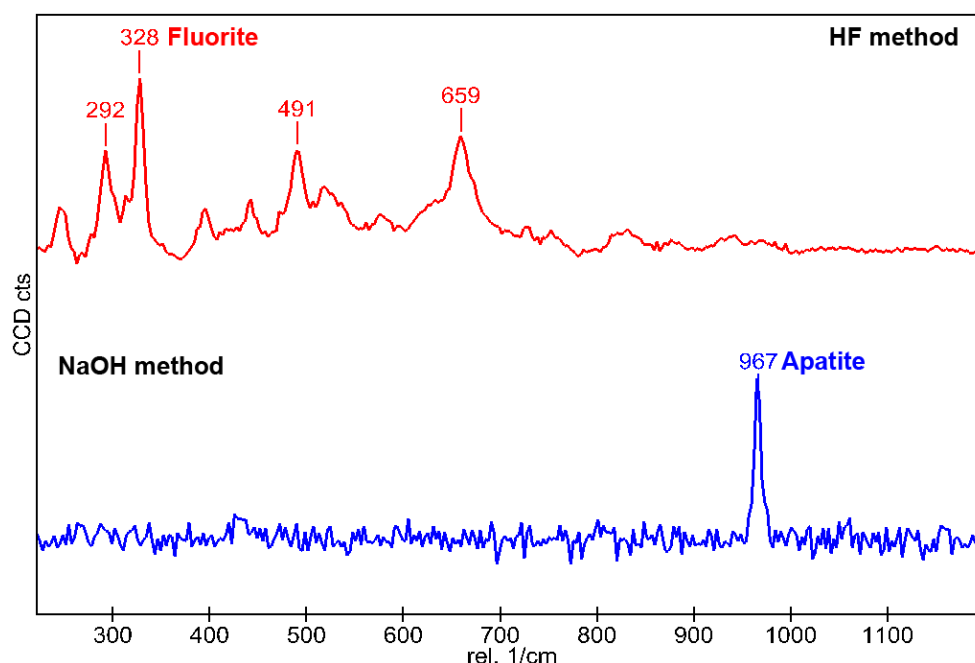


FIG. 5. Micro-Raman spectra of conodonts extracted respectively with HF acid (in red) and with NaOH solutions (in blue).

dissolution (Figs 1, 2), we suggest that the best solution to attack chert is at 3 M for 72 h, with a dissolution of c. 50% and 77% at 80°C for chert fragments of 1–10 mm and <1 mm respectively.

Compared to the standard method of microfossil extraction from chert using HF (hydrofluoric acid), the conodonts collected after rock digestion using soda were perfectly preserved in terms of mineralogy (i.e. still in hydroxyfluorapatite) as well as their external and internal ultrastructure features, such as growth lamellae.

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